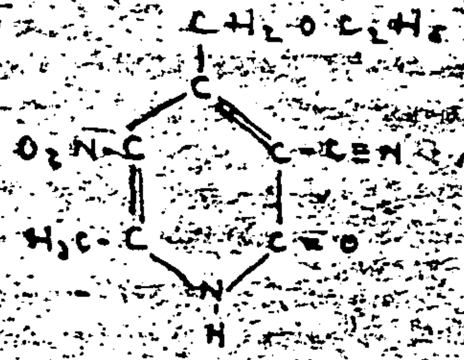
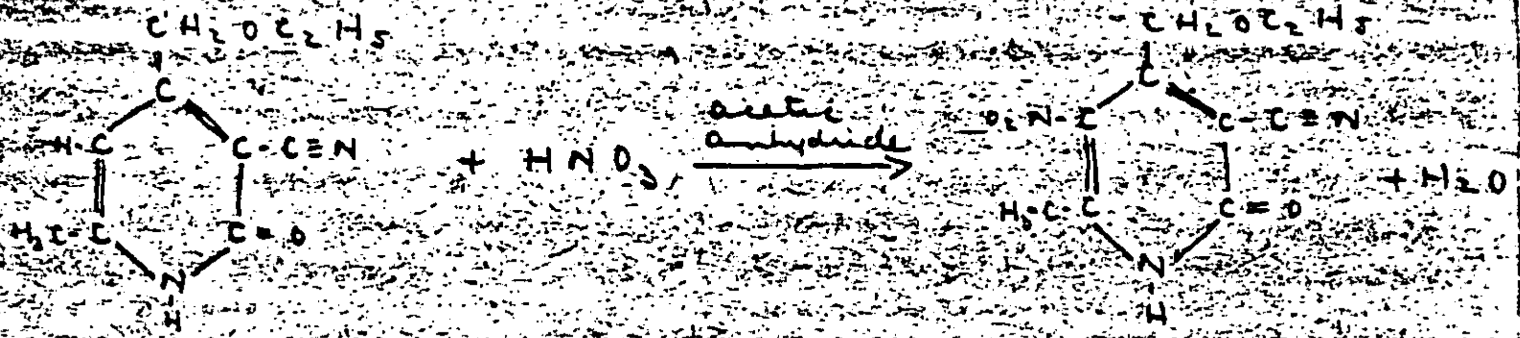
CAp-4 Bb



3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Pyridone

1. Reaction



3-Cyano-4-Ethoxymethyl-6-Methyl-2-Pyridone

3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Pyridone

2. Reactants

3-Cyano-4-Ethoxymethyl-6-Methyl-2-Pyridone

Nitric acid (Fuming)

3. Reagents

Urea

4. Yield

32%

5. Unit operations

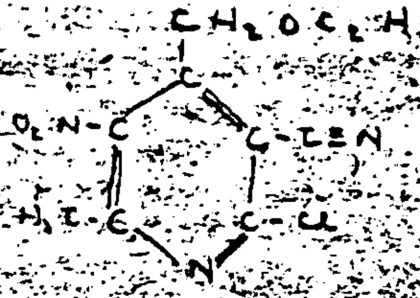
$A_{13} - D_2 - C_4 - I_1 - J_6 - L_5 - N_3 - P_{18}$

6. Solvents

acetic acid
acetic anhydride
Hydrochloric acid (37%)

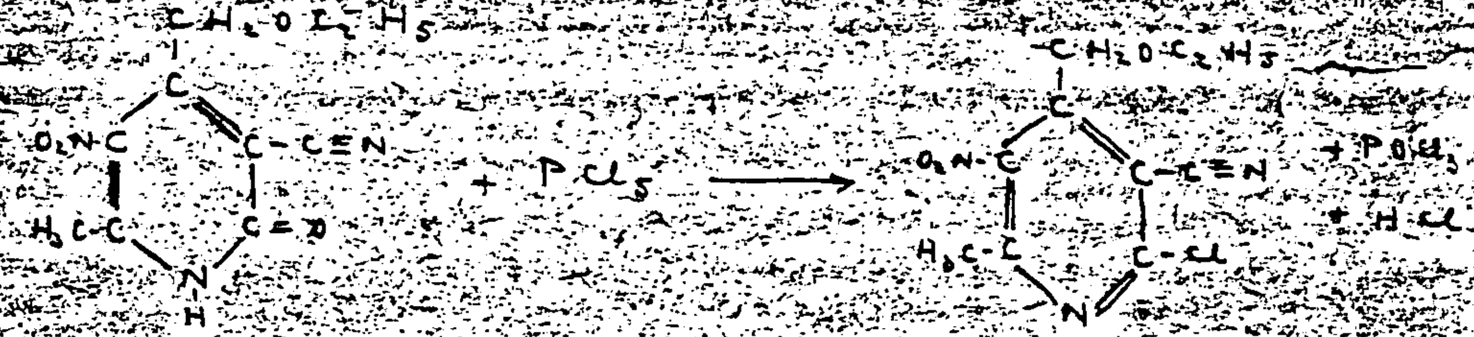
petroleum ether

Step 5 — D



3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Chloro-Pyridine

1. Reactions



3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Pyridone

3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Chloro-Pyridine

2. Reactants

3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Pyridone

Phosphorus Pentachloride

3. Reagents

None

4. Yield

41%

5. Unit Operations

A_{13} - B_2 - C_7 - D_1 - E_1 - H_1 - J_9 - L_4 - N_4 - P_{15}

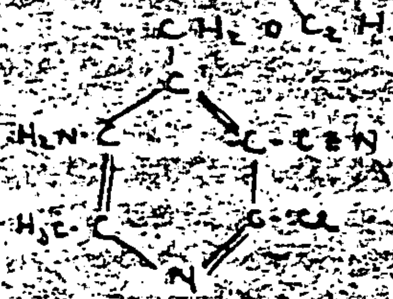
6. Solvents

Chlorobenzene

Ethyl alcohol (95%)

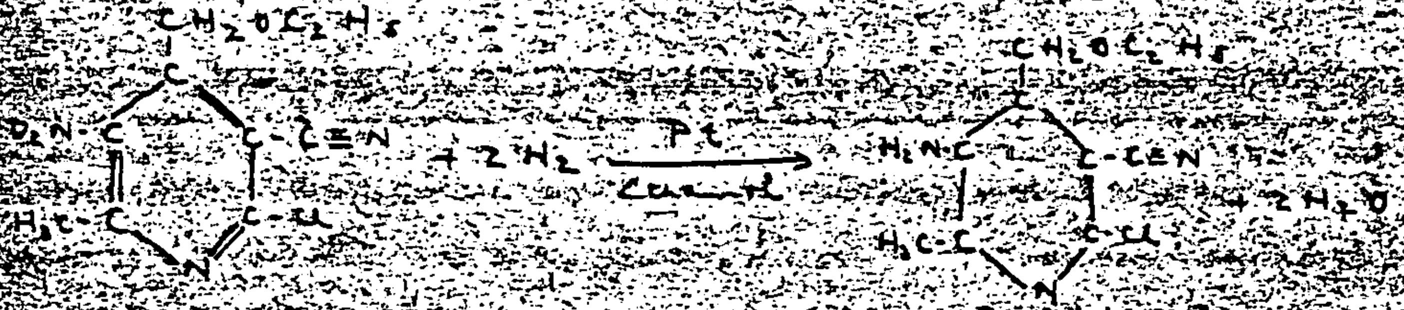
Petroleum Ether

Step 6



3-Cyano-4-Ethoxymethyl-5-Amino-6-Methyl-2-Chloro-Pyridi

1. Reaction



3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Chloro-Pyridine

3-Cyano-4-Ethoxymethyl-5-Amino-6-Methyl-2-Chloro-Pyridine

2. Reactants

3-Cyano-4-Ethoxymethyl-5-Nitro-6-Methyl-2-Chloro-Pyridine
Hydrogen

3. Reagents

Platinum (Catalyst)

4. Yield

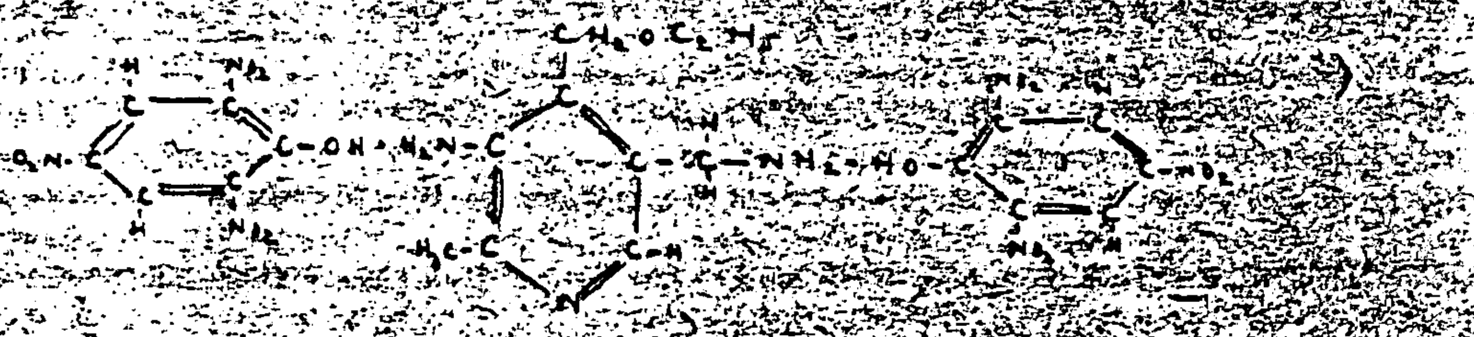
76%

5. Unit operations

$A_9 - B_2 - C_4 - D_3 - E_2 - G_1 - I_1 - J_9 - L_2 - N_4 - P_{13}$

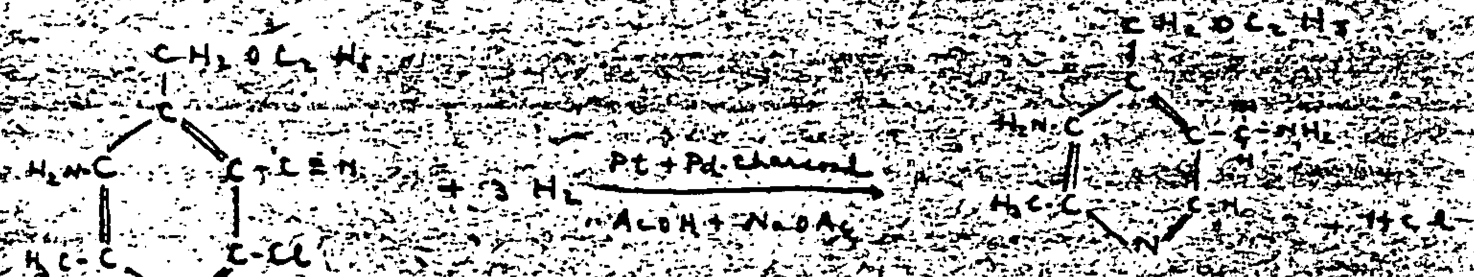
6. Solvents

Ethyl alcohol (95%)



3-Aminomethyl-4-Ethoxymethyl-5-Amino-6-Methyl-Pyridine-Dipicrate

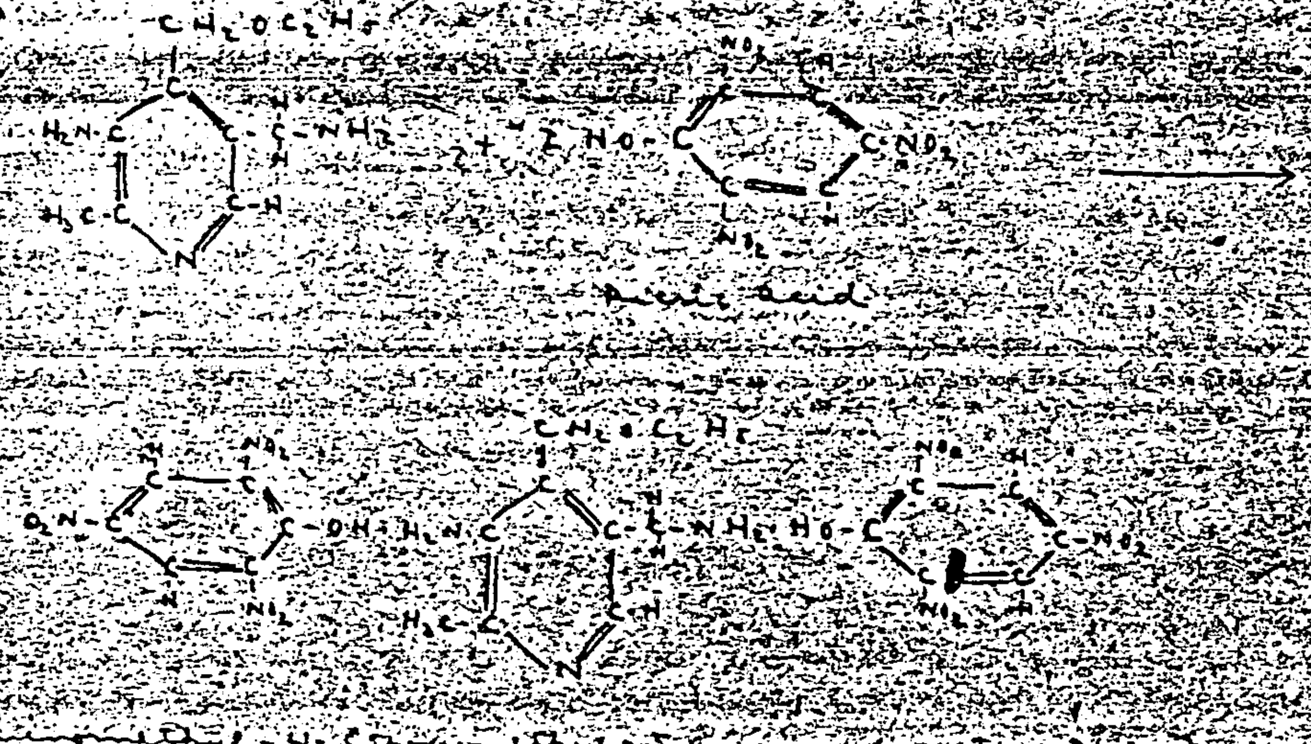
1- Reactions



3-Cyano-4-Ethoxymethyl-5-amino-6-Methyl-2-Chloro-Pyridine

3-aminomethyl-4-Ethoxymethyl-5-amino-6-Methyl-Pyridine

and,



Picric acid

3-aminomethyl-4-Ethoxymethyl-5-Amino-6-Methyl-Pyridine-Dipicrate

2. Reactants

3-Cyano-4-Ethoxymethyl-5-amino-6-Methyl-2-Chloro-Pyridine
Hydrogen
Picric acid

3. Reagents

Pt (catalyst)
Pd-charcoal (catalyst)
Sodium acetate

4. Yield

55%

5. Unit operations

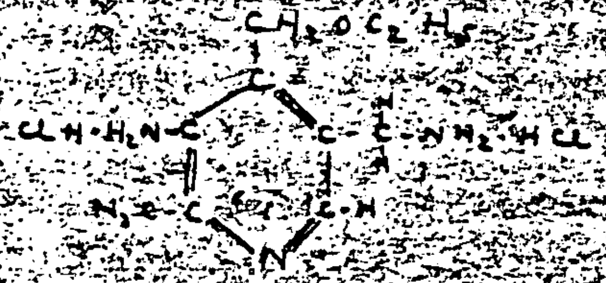
$A_6 - B_5 - C_1 - D_2 - G_1 - I_1 - J_5 - L_4 - N_4 - P_{10}$

6. Solvents

acetic acid
ethyl alcohol (95%)

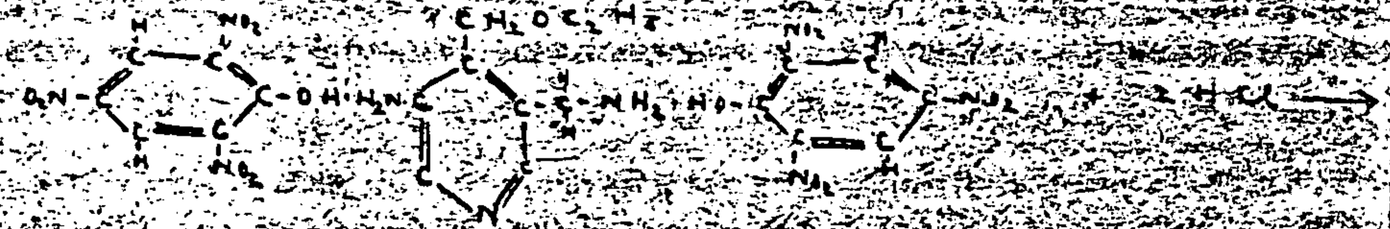
Step 8

B 6

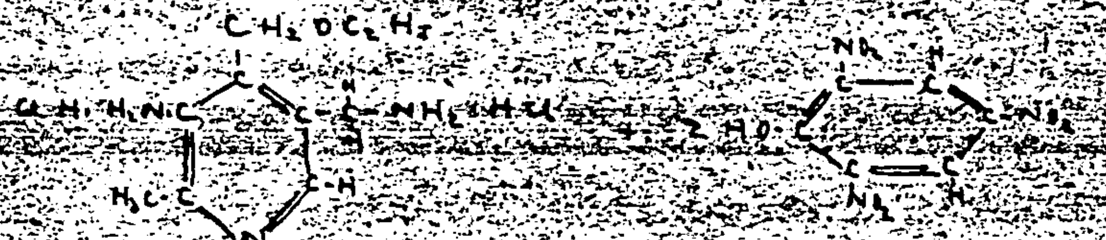


3-aminomethyl-4-ethoxymethyl-5-amino-6-methyl-pyridine-dihydrochloride

1. Reaction



3-aminomethyl-4-ethoxymethyl-5-amino-6-methyl-pyridine-dipicrate



Picric acid

3-aminomethyl-4-ethoxymethyl-5-amino-6-methyl-pyridine-dihydrochloride

2. Reactants

3-aminomethyl-4-ethoxymethyl-5-amino-6-methyl-pyridine-dihydrochloride

Hydrochloric acid

3. Reagents

None

4. Yield

76%

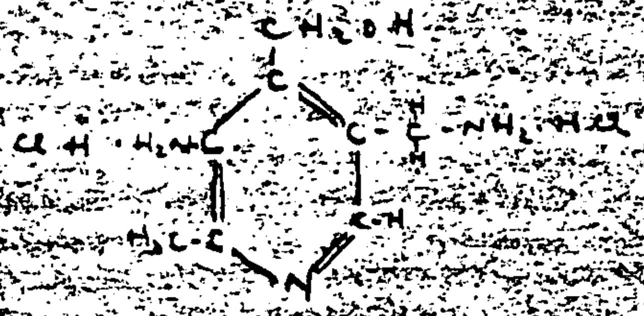
5. Unit operations

A_{15} - B_1 - C_4 - D_2 - E_2 - I_1 - J_{11} - L_2 - N_2 - P_{18}

6. Solvents

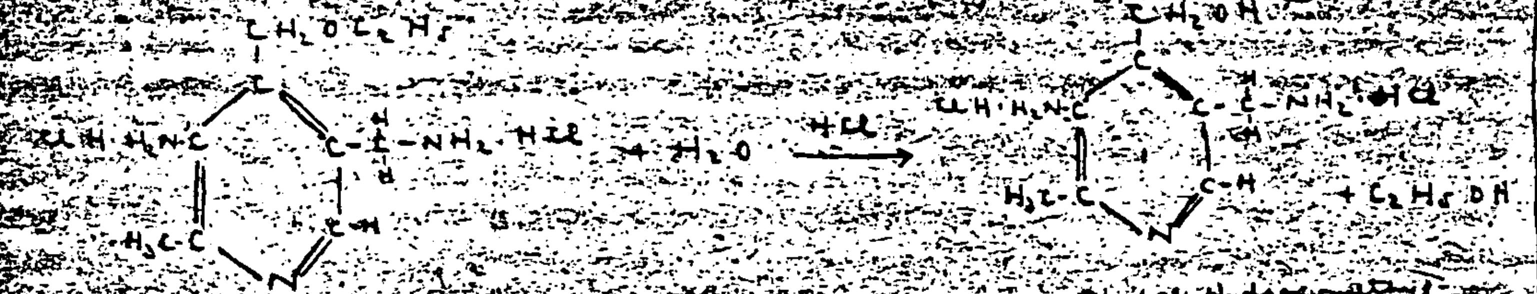
Nitrobenzene
Ethyl ether
Acetone
Ethyl alcohol (absolute)

Step 9



3-Aminomethyl-4-Hydroxymethyl-5-amino-6-Methyl-Pyridine-
Dihydrochloride

1. Reactions



3-Aminomethyl-4-Ethoxymethyl-
5-amino-6-Methyl-Pyridine-
Dihydrochloride

3-Aminomethyl-4-Hydroxymethyl-
5-amino-6-Methyl-Pyridine-
Dihydrochloride

2. Reactants

3-Aminomethyl-4-Ethoxymethyl-5-amino-6-Methyl-Pyridine-Dihydrochloride
Water

3. Reagents

Hydrochloric acid (2.5 N)
Activated Carbon

4. Yield

77%

5. Unit operations

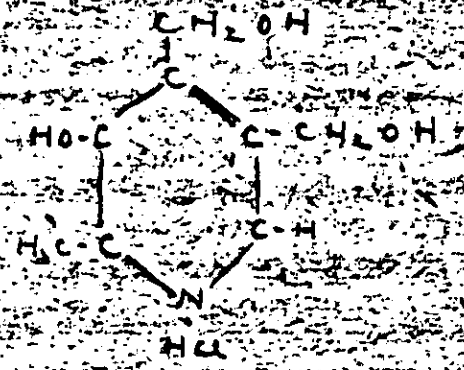
$A_4 - B_2 - C_3 - D_2 - I_1 - J_5 - L_2 - N_1 - P_5$

6. Solvents

Ethyl alcohol (31%)

Step 10

D6



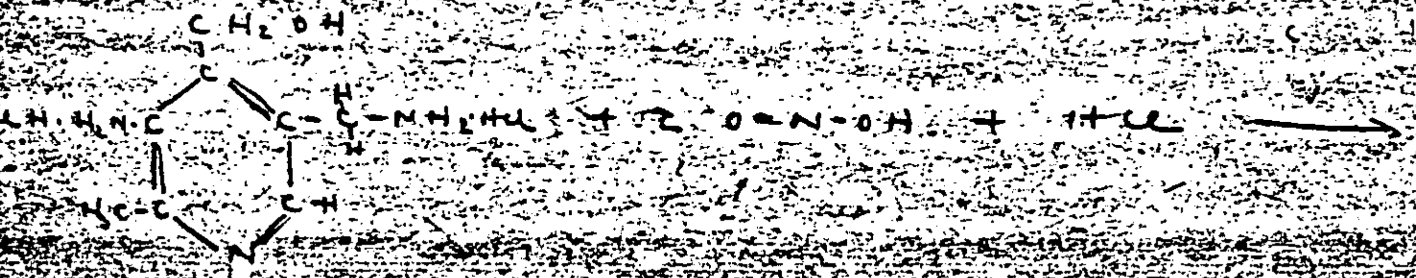
Peridoxin Hydrochloride
or
3,4-Hydroxymethyl-5-Hydroxy-6-Methyl-Pyridine-Hydrochloride

Reactions

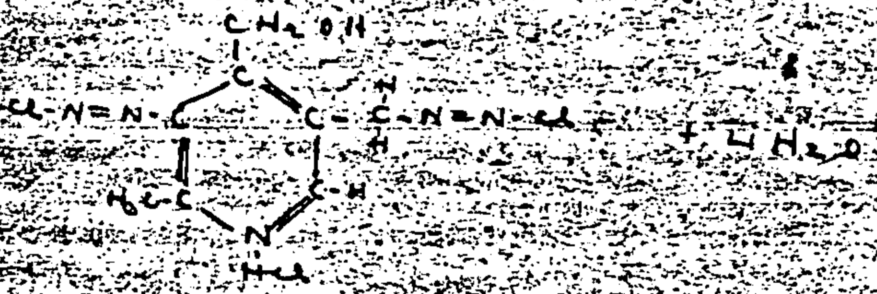
$$2\,NaO\text{-}N{=}O + 2\,HCl \longrightarrow 2\,HO\text{-}N{=}O + 2\,NaCl$$

Sodium Nitrite — Nitrous acid

and,

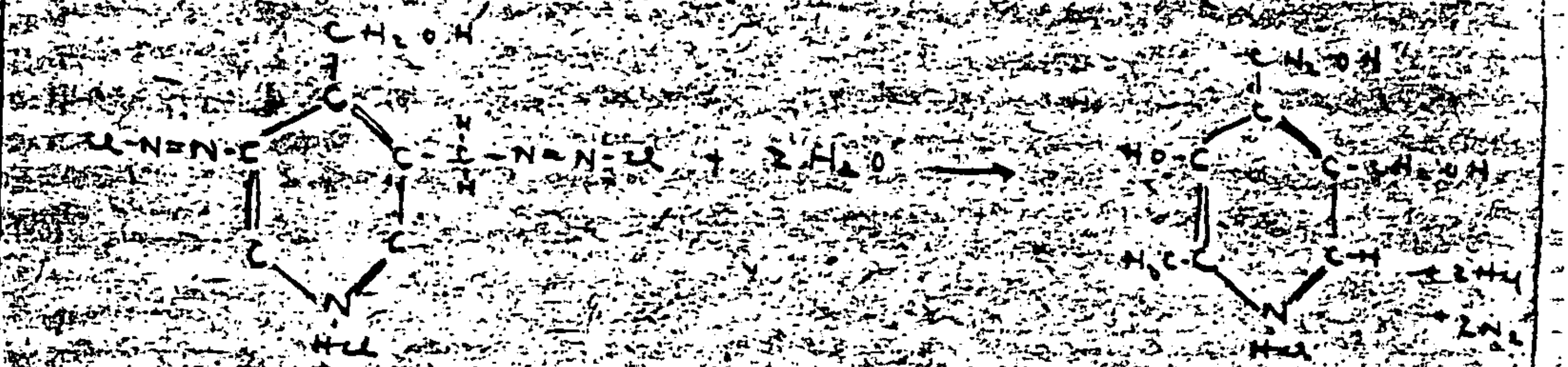


3-aminomethyl-4-Hydroxymethyl
5-amino-6-Methyl-Pyridine-Dihydrochloride



3-aminodiazonium chloride-4-Hydroxymethyl
5-Diazonium chloride-6-Methyl-Pyridine

finally,



Pyridoxine Hydrochloride

3, 4-Hydroxymethyl-5-Hydroxy-6-Methyl-Pyridine-Hydrochloride

2. Reactants

3-aminomethyl-4-Hydroxymethyl-5-amino-6-Methyl-Pyridine-Dihydrochloride
Hydrochloric acid
Water

3. Reagents

Sodium Nitrite
Hydrochloric acid

4. Yield

4.5 g.

5. Unit operations

$A_{10} - B_3 - C_3 - D_2 - E_1 - I_1 - J_{10} - L_2 - N_1 - P_{12}$

6. Solvents

Acetone
Ethyl alcohol (absolute)

cap 1

A 𝍸 𝍸 𝍸 𝍸
B ||
C 𝍸
D |||
E |||
G |
H ||
J 𝍸 𝍸 𝍸 |
L |
N |
P 𝍸 𝍸 𝍸 𝍸

cap 2

A 𝍸 𝍸 𝍸 𝍸 ||||
B |||
C |||
D ||
H |
J 𝍸 𝍸 ||
L |||
N |||
P 𝍸 𝍸 𝍸 𝍸

cap C 1 D6

A 𝍸 𝍸 𝍸 |||
B |||
C 𝍸 ||||
D |||
E |
H |||
J 𝍸 𝍸 |
L ||
P 𝍸 𝍸 𝍸

Grp 2	Grp 3	Grp 4	Grp 5
			-9
A 𝍸|	A 𝍸||	A 𝍸𝍸|||	A 𝍸𝍸𝍸𝍸||
B |	B |	B ||	B ||
C |||	C ||||	C ||||	C 𝍸|| → E |, D |, H |
I ||	I |	I |	J 𝍸||||
J ||	J |||	J 𝍸|	L ||||
L ||	L |	L |||	N |||
N ||	N |	N |||	P 𝍸𝍸𝍸
P 𝍸|	P 𝍸||	P 𝍸𝍸𝍸	

Materials Cost

[illegible] acetic acid	278.10 (267.20)
ethyl alcohol (absolute)	243.60
Sodium	743.32
HCl (36%)	274.54 (337.89)
HCl (gas)	56.40
Na_2CO_3	124.26 (117.?)
NH_3 (aqueous, 28%)	36.52 (44.10)
acetic acid (glacial)	120.60
HNO_3 (fuming)	42.55
acetic anhydride	23.37
urea	2.58
piperidine	4.71
$CuSO_4$	~~15.20~~ 15.58
Sodium acetate	2.76
Pt catalyst	0.37
Pd(5%)-charcoal catalyst	7.33
Hydrogen	0.45
PICRIC ACID	1.77
PCl_5	28.18
$NaNO_2$	4.54
activated carbon	0.35
~~PICRIC ACID~~ NaCN	34.54

[illegible] → D.

$\frac{240.0}{285.6 \times (0.43)}$ × [illegible] = 2.59 # [illegible] HCl

$\frac{[illegible]}{[illegible]}$ × 2.59 = 2.90 # HCl

$\frac{[illegible]}{[illegible]}$ × 3.[illegible] = 4.34 # $NaNO_2$

[illegible] and [illegible]

$\frac{230.1}{240.0 \times (0.77)}$ × [illegible] = 3.93 # 4-[illegible]

$\frac{[illegible]}{[illegible]}$ × 3.93 = 14.40 # HCl

$\frac{0.2}{[illegible]}$ × 3.93 = 0.38 # activated C

[illegible]

[illegible] → 4-[illegible]

$\frac{[illegible]}{289.1 \times (0.6)}$ × 3.93 = 72.07 # [illegible]

$\frac{57}{376}$ × 72.07 = 10.94 # HCl

[illegible] → [illegible] cpd

$\frac{225.6}{653.3\times(0.58)} \times 12.07 = 7.53$ # 5-[illegible] cpd

$\frac{11.3}{31} \times 7.57 = 2.76$ # NaOAc

$\frac{0.5}{31} \times 7.57 = 0.12$ # Pt catalyst

$\frac{30}{31} \times 7.57 = 7.33$ # Pt-alumina catalyst

$\frac{0.70}{31} \times 7.58 = 0.88$ # H

$\frac{70}{31} \times 7.58 = \frac{17.70}{3.54}$ # picric acid

Step 6

5-Nitro cpd → 5-amino cpd

$\frac{255.6}{225.6\times\boxed{0.78}} \times 7.59 = 11.31$ # 5-Nitro cpd

$\frac{0.5}{22} \times 11.31 = 0.26$ # Pt catalyst

$\frac{0.52}{22} \times 11.31 = 0.27$ # H_2

Step 7

Piperidine → Piperidine cpd

$\frac{237.1}{255.6\times(0.41)} \times 11.31 = 25.60$ # Piperidine cpd

$\frac{66}{60} \times 25.60 = 28.78$ # Pd [illegible]

Formation of 5-nitro[illegible]

$\frac{1911}{237.1 \times (0.32)} \times 2560 = 64.40$ # 5-H [illegible]

$\frac{13.7}{5} \times 64.40 = 176.4$ # AcOH

$\frac{3.3}{5} \times 64.40 = 42.55$ # HNO_3 ([illegible])

$\frac{2.2}{5} \times 64.40 = 28.3$ # Acetic anhydride

$\frac{0.2}{5} \times 64.40 = 2.58$ # Urea

Step 3

Ethyl acetyl acetone → Piperidine

$\frac{144.1}{199.7 \times (0.91)} \times 64.40 = 60.00$ # Ethyl acetyl acetone

$\frac{7.3}{93.1} \times 60.00 = 4.71$ # Piperidine

$\frac{6.3}{93.1} \times 60.00 =$ [illegible]

Step 2

Ethyl ethyl acetate → Ethyl acetyl acetone

$\frac{143.1}{144.1 \times (132)} \times 60.00 = 192.80$ # ethyl ethyl acetate

$\frac{37}{132} \times 192.80 = 54.05$ # acetone

$\frac{25}{132} \times 192.80 = 36.52$ # Na

$\frac{60}{148.1} \times 1.11 \times \frac{192.80}{2} = 44.20$ # AcOH

$\frac{159.3}{141.8} \times 1.5 \times \frac{192.80}{2} = 158.80$ # $CuSO_4$ anhydrous

$= 244.0$

$\frac{94.1}{138.1 \times (0.86)} \times 172.70 = 219.40$ # [illegible]

$\frac{1250 \times 0.791}{142} \times 219.40 = 1527.80$ # EtOH ([illegible])

$\frac{69}{142} \times 219.40 = 106.70$ # Na

$\frac{180 \times 0.791}{142} \times 219.40 = 220.60$ # EtOH ([illegible])

$\frac{149 \times 1.19}{142} \times 219.40 = 273.90$ # HCl

$\frac{230 \times 0.791}{142} \times 219.40 = 281.04$ EtOH

$\frac{36.5}{142} \times 219.40 = 56.40$ # HCl

$\frac{53 \times 1.11}{36.5} \times 56.40 = 90.40$ # Na_2CO_3

$\left\{ \frac{92}{94.5} \times 219.40 = 213.60 \right.$ # [illegible] $\left. \right\}$

Stage P-2

Et cyanoacetate → Cyanoacetamide

$\frac{113.1}{144.1\ (0.77)} \times 60.05 = 54.15$ # Et cyanoacetate

$\frac{500 \times 0.9}{500} \times 54.15 = \overset{44.70}{\cancel{26.52}}$ # NH_3 ([illegible])

Stage P-1

$\frac{94.1}{113.1\ (0.77)} \times 54.15 = 58.70$ # [illegible]

$\frac{290}{500} \times 58.70 = 34.06$ # Na_2CO_3

([illegible])

$\frac{[illegible]}{600} \times 5570 =$ [illegible]

$\frac{674}{500} \times 5570 = 8140$ [illegible]

6635

46.15

HRC [illegible]
[illegible] 1278
[illegible] 791

$\frac{1431}{160} \times 0.9$ [illegible]

[illegible]
1670

2.66

9.1
9.1
C [illegible].0
N 42.0
O 16.0
H 13.0
653.

10 [illegible]
N [illegible]
[illegible]
344
[illegible]
21.00
[illegible]
25.47

[illegible] C [illegible]
N 14.0
[illegible]
[illegible]
11 H [illegible]
N [illegible]
2 O [illegible]
197.0

13 C 13[illegible].0
3 N 42.0
Cl 70.91
10 O 16.0
19 H 19.02
79.93

8 C 96.0
1 N 14.0
3 O 48.0
[illegible]
17 H 17.01
0.593

10 C [illegible]
3 N 42.0
3 O 48.0
1 H [illegible]
[illegible]
239.5

10 C [illegible]
3 N 42.0
1 Cl 35.5
1 O 16.0
12 H 12.0
[illegible]

8 C 96.0
3 N 42.0
2 Cl 70.91
1 O 16.00
15 H 15.01
[illegible]

[illegible] C [illegible]
3 N 42.0
4 O 64.0
11 H 11.0
237.0

7 C 84.0
3 O 48.0
12 H 12.0
144.0

6 C 72.0
4 O 64.0
1[illegible] H 1[illegible]
[illegible]

2 C 24.0
[illegible]
3 H 3.0
1 Cl 35.5
94.5

$\frac{32}{144.1} \times 1.11 =$ 3349 Acc H $\frac{}{60}$

$\frac{177}{[illegible]} \times 1.8 =$ 2.504

$\frac{60}{144.1} \times 1.7 =$ .7 [illegible] 445

1448

43

[illegible]

70[illegible]

216.30
56.90
21.90
14.40
18.44

327.94

327.94
36.40

291.54

[illegible]
6.53

32.89

$\frac{144}{14.4} =$ 219.40

219.40
58.70

278.10

90.20
34.26

124.46

tickets

90

213.60

106.80
36.52

143.32

176.40
[illegible]

120.60

219.40
47.80

267.20

90.20
27.71

1297

OV
6/6/5

#14

148g. KOH 85% $\frac{}{72}$ 16.5g. KOH
3.[illegible] KOH

500cc. Kerosene
73-75 CaC_2 $\frac{75}{12} = 6.5$ 13g CaC_2

58g. acetone
425cc. methylal
300g. ice

3

$\frac{33}{97} \times 500 = \boxed{84}$ Kerosene

1.4 × 0.045 = 0.0[illegible]

#15

$$X_n = 28\left(\frac{\overset{137}{\cancel{265}}\times 530}{\overset{137}{\cancel{265}}\times 530+25}\right)^8$$

$$\cancel{28}\left(\frac{196}{221}\right)^8$$

$$28(.89)^8$$

$$\begin{array}{r} 28 \\ 17.6 \\ \hline 16.4 \end{array}$$

9.95 − 10

7960 − 80

1.60

#16

1000 - 200g/24 hrs 32 / 0.4

1000/½ lb 14.2 / 7.1 1. 12.8 / 25.6

480,000 6.4 32.4

34.4 g = 0.2 mole lactide

7.1 g. = 0.05 mole P_2O_5

2.7 g. = 0.15 " H_2O

38.4 g. = 1.2 mole MeOH

48 g. 50 cc.

Restilled of C_6H_6
bp w
I 80-100
II 110-125 1g n_D^{24} 1.4160
III 135 10.5g n_D^{25} 1.4112
Crystallized with H_2O
8g. residue

R+H MeOH i-butyrate
n_D 1.4100

Time	Pot Temp	Reflux T
2:15	71°	63
2:45	75° (H_3PO_4 in alc'n)	63.5
2:50 took off 10 cc	80°	64°
2:53 Took off 20 cc	87°	64°
3:00 " " 25 cc	95°	64°
3:20	92°	64°
3:25 " " 30 cc	105°	64°
5:00	104°	63.8
4:15 took off 35 cc	125°	64°
4:50	125°	63.7
5:50	125.5	63.2
6:45 PM	130	62.4
2 AM	135	61.3

a.at.t. 21.0075
3/17/42
2.6g neutral extract
8.3g. H_2O approx.
Distilled small amt
material at ca. 130°/20 mm
until 140-180°, Cryst'd
in condenser

Please let this reflux overnight, Harry A

6:45 PM Took off 1cc went to 64 - 1.40

11 AM 133° + 61-2 Phil

236 g (2 mole) -OH ester
42 g. (0.67 mol) H_3BO_3
80 cc. C_6H_6 + 30 in trap on top of column
OH ester clouded on adding C_6H_6

4 cc. H_2O distilled readily with C_6H_6 (pot temp to 90
Then no more H_2O but material which floated on top of C_6H_6

Replaced trap by still head + distilled over moist 80 cc. C_6H_6 layer + ca 30 cc. other mat. (pot temp 90-150°) Material came over a low boiling azeotrope.

Cont'd distn with still pot temp remaining at 150° during most of distn + finally rising to 170°. Some polymer formed in column. Temp of vapor varied from 60-95° depending on reflux rates. High reflux ratio gave lowest temp. Collected ca. 130 cc. distillate which reduced $KMnO_4$ + partially immiscible with H_2O

The 130 cc was dil'd with 40 cc. H_2O before clouding. Added total 90 cc. H_2O with no sep'n only cloudy. Added 80 cc. pet ether with poor sep'n. Sol'n 2[illegible] g. salt gave good sep'n. Ext'd H_2O layer with 20 cc. add'n pet ether. Total pet ether sol'n washed with sat'd salt sol'n. Same salt sep'd

A.I. phase distilled → 27 g. b.p. 55-6 n_D^{20} 1.3590
(n_D^{24} acetone 1.3589)

4/21/48

120 g. OH ester heated with 115 g. NH_4HSO_4 with stirring - column. Pot temp 140-5 for most of expt. Rose to 170-5° at end. Distillate 60-103 depending on rate of takeoff. Of 95 cc. distillate, all except last 10-15 cc. (b.p. 79°) was clear ~~at~~ Last few cc. 2-phase. 84 g. distillate. Loss in weight of still pot 101 g. Total time ca 7 hrs.

Distillate ~~faintly cloudy~~ → single layer on dil. with 80 cc H_2O. Added 25 cc pet ether + sep'd.

Dist'n aq. layer →

1.6 g. b.p. 56-60°

16.8 g. 60-65 (Some H_2O insol. mat. probably methacrylate)

Small amt. polymer formed in still pot soon after dist'n begun. Aq. residue strongly acid (ca. pH 4) requiring 22 cc. 0.3054 N NaOH to neutralize to phenolphthalein.

#17

Passed in C_2H_2 → rise from 20°–35° & holding at 35° for 1 hr.

added acetone 17.7 gms. @ 15°C. Some slight steady rise obtained. Reacted for 5 hrs. at 13–15°C.

Decomposed at 2°C with 150 cc HOH.

Separated two layers – bottom (HOH) only 105 cc. added solid CO_2 → ppt. (of K_2CO_3?)

Separated AmOH (washing ppt. twice with AmOH)

Washed AmOH soln. once with HOH (equal vol.)

adjusted pH to 6.0

Distillation

	Pot.	Lower col.	Upper col.	Press. mm Hg.	Notes
	35	—	—	50	
	40	35	—	50	distillate 90 cc (80 cc HOH)
	50	40	—	50	
	Kicked over twice – badly (carried HOH & [illegible])				
	51	40	31	50	
	72	64	63	50	
1.7 .9 5.9	72	64	63	50	150 cc AmOH pH 6.9 adj to 6.6
				50	
4.2	74	66	65		pH 6.9 adj to 6.6
1.1 5.1	74	68	66	50	
1.6	75	69	67	50	
[illegible] [illegible]	76	70	69	50	pH 6.7 adj to 6.2

see
29/9

0.328

0.164(80) = 13.12

Tare 245.9

355.5 plus Camph.H

66.0

421.5

Distillation Record

Flask	L.C.	V	Variac 60-71-75-78
167	128	90	-80
167	128	92	
169	129	94	
173	131	93 — KOH setting	
176	131	92	
178	131	94	
180	133	103	
186	134	120	

Reflux 8^{30} 11^{30} — 3 hrs.

add acetone 11^{30}

reacted 11^{30} $2\frac{00}{AM}$ 2½ hrs.

-15° Same rule

$$\begin{array}{r} 102.4 \\ 54.1 \\ \hline 48.3 \\ 10.0 \\ \hline 38.3 \\ \hline 0.815 \end{array}$$

#18

Arthur H. Thomas (2)

HR-108 Rubber Stoppers

8808 – Twohole with 2 fusiform, funnel top openings

1 doz.	# 00	$0.21
1 "	0	.33
1 "	1	.37
1 "	2	.39
1 "	3	.45
1 "	4	.48
1 "	5	.54
1 "	5½	.57
1 "	6	.62
1 "	6½	.67
1 "	7	.79
1 "	8	.90

9766 – Tygon tubing, Tygon S22-1

1 carton – 10 ft 3/16" bore $0.18/ft less 10%

1 carton – 50 ft 1/4" bore $0.27/ft less 15%

#19

Continuation Sheet 5

B_1 (Thiamin) was assayed for by the yeast-growth method of Schultz, Atkin and Frey.

b- Considerable work was done on the development of special cultures suitable for increasing the Riboflavin, Niacin and Pantothenic acid content of the recovered by-product yeast. This research was successful and resulted in feed values 200 to 300% in excess of what they had previously been.

c- Some original investigations were completed on assay methods for Biotin and Folic acid as present in feed yeast; these factors of the B complex had then only recently been discovered.

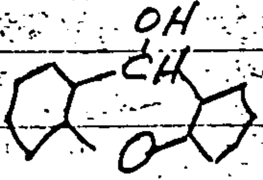
1. Period   April 1942 to February 1946

#20

C(- 1914 158, 1076, V88; 159, No

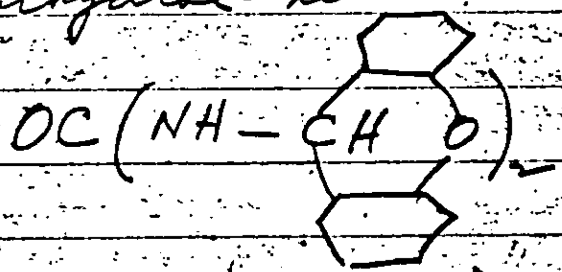
R. Fosse *E.O. I 476

In the presence of a little acetic acid urea combines with Xanthydrol



to give the very stable

dixanthydrol-urea



$OC(NH-CH\ O)_2$

which is completely insoluble in acetic acid water, and cold alcohol. The estimation is by weighing the precipitate, or a volumetric modification devised by F. W. Allen and J. M. Luck (J. biol. Chem., 1929 82, 693

Organic Chemistry of Nitrogen

POD Taylor + Baker pp. 280-

Oxford 1937

#21

TRANSLATION FROM THE FRENCH

Mode of operation A

The solution of urea is increased first with 35 times its volume of acetic acid, then with its half volume of alcoholic xanthydrol.

After one hour the white boiled mixture, crystallized, is dried in the air, washed in alcohol, dried, weighed and analyzed.

Titer in urea(1)

Theory	found →
5 g	4.93 g 4.955 4.934
2 g	2.04
1	1.0085 1.011

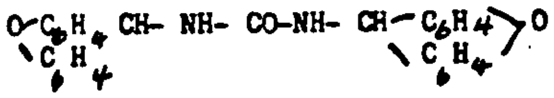
If one compares the results of the analysis with the solution of urea in the amount of 5 grammes with those of less concentrated liquids which follow, one notes that the mistake made changes its indications. While it is defective and fluctuates around -1 per cent for the titer of 5 grammes, it rises to $2 per cent for the liquid in the amount of 2 grammes. The explanation of this fact, which may seem quite remarkable a priori, is given us by the analysis. The latter establishes that the percentage in nitrogen of urine decreases slightly and hence its purity also when the proportion of of the xanthydrol to urea increases in the reactionary mixture.

****

Z.Lyon

TRANSLATION FROM THE FRENCH

These results, due to the xanthydrol, spring from the formation of a definite compound, crystalized, very little soluble and seven times higher in molecular weight than that of urea:



$$O{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}CH-NH-CO-NH-CH{<}\begin{matrix}C_6H_4\\C_6H_4\end{matrix}{>}O$$

Xanthydrol is just as valuable for the quantitative analysis of urea. The new method which is based on its use differs essentially from those which are in usuage by its principle and the control to which it admits.

Instead of destroying the carbamide and restoring its proportioning to the measure of its products of decomposition, we convert it almost quantitatively into its characteristic dixyanthin derivat which we weigh.

Composition of the medium used for the proportioning of urea

Titrated solution of urea	1 cm	20 cm
Crystallizable acetic acid	3.5	70
Xanthyrol liquid in the amount of 1/10 in pure alcohol	.5	10
	5.0	100

* * *

z.l

Mode opératoire A

La solution d'urée est additionnée d'abord de 35 fois son volume d'acide acétique puis de son demi-volume de Xanthydrol alcoolique.

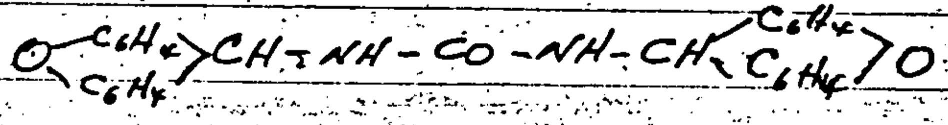
Après 1 heure, la bouillie blanche, cristallisée, est essorée, lavée à l'alcool, séchée, pesée et analysée.

Titre en urée (l.)

Théorie	Trouvé
5g	4.939 4.955 4.984
5 g	5.04
2	
1	1.0085 1.011

Si l'on compare les résultats du titrage de la solution d'urée à 5 g avec ceux des liqueurs moins concentrées qui suivent, on ~~constate~~ constate que l'erreur commise change de signe. Tandis qu'elle est défaut et oscille autour de - 1 pour 100 [illegible] elle s'élève à +2 pour

Ces résultats, dus au xanthydrol, découlent de la formation d'un composé ~~fu~~ défini, cristallisé, fort peu soluble et de poids moléculaire sept fois plus élevé que celui de l'urée:



$$O\begin{matrix}\diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup\end{matrix}CH-NH-CO-NH-CH\begin{matrix}\diagup C_6H_4 \diagdown \\ \diagdown C_6H_4 \diagup\end{matrix}O$$

Le xanthydrol n'est pas moins précieux pour l'analyse quantitative ~~de~~ de l'urée. La nouvelle méthode, qui repose sur son emploi, diffère essentiellement de celles qui sont en usage par son principe et le contrôle dont elle est susceptible.

Au lieu de détruire la carbamide et de ramener son dosage à la mesure de ses produits de décomposition, nous la transformons presque quantitativement en son dérivé dixanthylé, caractéristique, que nous pesons.

Composition du milieu employé pour le dosage de l'urée

Solution titrée d'urée	1 cm³	20 cm³
Acide acétique cristallisable	3.5	70
Liqueur de xanthydrol à $\frac{1}{10}$ dans	5	10

1.16|50

100 pour la rigueur à 2g. L'explication de ce fait, qui peut paraître assez singulier, *a priori*, nous est donnée par l'analyse. Celle-ci établit que la teneur en azote de l'uréine décroît légèrment et par conséquent aussi sa pureté, lorsque le rapport du xanthydrol à l'urée augmente dans le mélange réactionnel.

#22

11-26-[illegible]

Time	$Ca(OH)_2$ added	Temp	Notes
7 30	10	15	
7 35	5	16	
7 40	5	17	
7 45	5	15	
7 50	5	15	
7 55	10	18	almost all $Ca(OH)$ gone
8 00	5	15	
8 05	5	12	
8 10	—	14	Finish

Filter 8 20 — Residue

Draw off Cl_2 9 00 — 5 gms wet = 2 gms dry

Titration

$\frac{200}{0.4} \times 1.5 \times 0.1047 \times 0.0358 = 1.1$ gm. $Ca(OCl)_2$

M.W.

$Ca(OH)_2$ = 74

$Ca(OCl)_2$ = 143

Tert amyl OH = 88

Tert Amyl O Cl = 123.5

$4\overline{)143}$
35.75

87
35.5
122.5

$2Ca(OH)_2 + Cl \rightarrow Ca(OCl)_2 + CaCl_2$

$35 \times \frac{74}{100} = 27$ gm. $Ca(OH)_2$

$50 \times \frac{74}{100} = 40$ gm.

Titration for $Ca(OCl)_2$ in

$10.5 \times 0.1047 \times 0.03558 = 0.0393$ g.
×00

$\frac{200}{0.4} \times 0.0393 = 15.7$ gms.

1 gm produces $\frac{143}{2 \times 74} \times 1 = 0.97$ gm. $Ca(OCl)_2$

11^{10}	10
11^{15}	5
11^{20}	5
11^{25}	5
11^{30}	5
11^{35}	5
11^{40}	5
11^{45}	5

30
60

Hercules Schenkweiler 3 / DuPont 2

PE 6-6268 / Orensky ST8-2020

20 . 060
120

$$\begin{array}{r} 45 \\ -10 \\ \hline 35 \end{array}$$

200

35 - 33.9 = 1 liter

3 ~~2~~
~~5~~
150 x 33 =

$ROCl + Ca(OH)_2 \rightleftarrows \boxed{ROH} + Ca(OCl)_2$

$\longleftarrow$

1020

38.4   48.2
14.9   38.4
18.5   9.8 | 100 114

250
2.54
3.6

$2Cl_2 + 2Ca(OH)_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2H_2O$

2×71   2×74   143   111   2×18
142   148   2
296

av Cl - 25 gpl → $Ca(OCl)_2$

1.6[illegible] – 0.1[illegible] = 0.0[illegible]93

0.[illegible]03

6/6/50

215

$C\,C_s \times N_s \times$ [illegible] = [illegible] Y

$44.1 \times N_s \times .04903 = 0.2$

$$N_s = \frac{0.2}{44.1 \times 0.04903}$$

20

cc × N × mEq = amt X

~~8.6 × 0.1025 × 0.04962~~ ~~4.4 × 10~~

~~[illegible]~~ 0.044 g

$$\frac{0.044}{1}$$

0.246

~~78%~~ → 1.8% as $Ca(OCl)_2 \cdot 3H_2O$

~1.9

$Ca(OH)_2$

$$\frac{74}{197} \approx 21$$

7.6

cc × N × (mEq) = amt X

8.6 × (0.1025) × 0.0493 = 0.044 am

$Ca(OCl)_2 \cdot 3H_2O$

1650.

2

22/6

0.2

Ca OCl OCl + 2HCl → Ca

Cl2 + ...

Cu

7.0 + 0.0047

0.0343

0.0261

CaCO3

→ Ca(OCl)2

2 G+ 1

5/46

$3 \times 0.3 \times \frac{220}{2} \times \frac{74.10}{176} = \boxed{5.6}$

$Ca(OH)_2 + ROCl \rightarrow$

79.5
62
17.5
1400 gms

36 gms

$\frac{8}{9} \times 35 =$ Extra ROCl

Extra ROCl $\times 0.90 \times \frac{74.10}{176}$

$= 2ROCl : CaOH$

$Ca(OH)_2 - 3H_2O$
$74 : 54$

$5.6 \times \frac{54}{74} = \boxed{4.1 \text{ cc}}$

75

$CaCO_3$ — Molar 100

39 $Ca(OCl)_2$ — 143 1

35.5 g/L avCl₂ = NSOA

40 → 143

$\frac{143}{2\times100} \times 50 = 27.6\,g$ $Ca(OCl)_2$

89 $\frac{17.6}{143} \times 27.6 = 35.2\,g$

~~31.3 g~~

0.89

3.4

$\frac{1000}{250}$

$\frac{750}{250}$

$2CaCO_3 + 2Cl_2 \rightarrow Ca(OCl)_2 + CaCl_2 + 2CO_2\uparrow$

100 71

$Cl_2 \rightarrow HCl + HOCl$

~~24 — 143~~

~~48~~

1

50 35.5 — 0

40

44
22.4 lit

~~17.1 liter~~

28 gms

200 143 58

40 39/20

$36 \times \frac{143}{2 \times 100} = 25.7\text{ g } Ca(OCl)_2$

$\frac{7}{9} \times 25.7 = 22.7\text{ g } Ca(OCl)_2$ extd

$22.7 \times 0.90 = 20.4\text{ g } Ca(OCl)_2$

$20.4 \times \frac{74}{143} = 10.6$

5.6

/11

$\overset{36}{2} CaCO_3 + Cl_2 \rightarrow \overset{1}{Ca(OCl)_2}$

#23

Sodium Peroxide	4	oz
" Bismuthate	1	"
Ammonium Oxalate	4	"
Potassium Chromate	4	"
Potassium Thiocyanate	4	"
Potassium Chromate	4	"

~~Dr. Mr. W[illegible]ch Di 3-4900~~
~~Belmont Smelting + Refining~~ Works

☐

E+A 11-830 Labels rectangular, gummed with red border
2 boxes size 217 0.20
3 boxes " 205 0.30
11-676 Ice-Chipper 1.00

Silicone grease - 2 tubes

14-357 Scoopula - Box of 6 $1.00

6/6/50
mo

Chemicals to order (Minimum quantities)

~~Potassium mercuric-thyocyanate~~
~~Cobalt nitrate~~
~~Magnesium chloride~~
~~aurin tricarboxylic acid reagent~~ (for Al deter.)

FA 9-528 Rheostat Size H (20 ohm) $8.00
~~9-506A Weston ammeter 0-10 amps $9.00~~
~~9-506C Weston voltmeter 0-5 volt 12.00~~ 0-25
2-535 Battery porous cups

2 Size #1 $0.32
2 " " 5 0.52
1 " " 7 0.54

2-587 Beaker, nickel 250cc. 3.00
2-592 Beaker, monel metal 250cc. 4.00

Vill Corp 1076 Weston Model 280 Volt ammeter
50/5/2.5 volts 10/1/0.1 Amp 32.25
FA 10-001 Finger Cots, light rubber
1 doz. med. 0.50
1 doz large 0.50
9-191-5 1 pkg (200cc) 6 mo, Bel [illegible] 3.25
2-540 Beaker, Griffin with spout, Pyrex
1.20 1.02 1.62
6 - 10cc. 6 - 30cc. 6 - 50cc.
8-125 Crucible, Plumbago without cover, size #2 (375cc) 1.00
Sue

#24

$$R'\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}R' \rightleftarrows [R'COO]$$ ✓

$$R'COO \longrightarrow \boxed{R'^{+}} + CO_2$$

$$R'^{+} + R'COO \longrightarrow R'COOR'$$

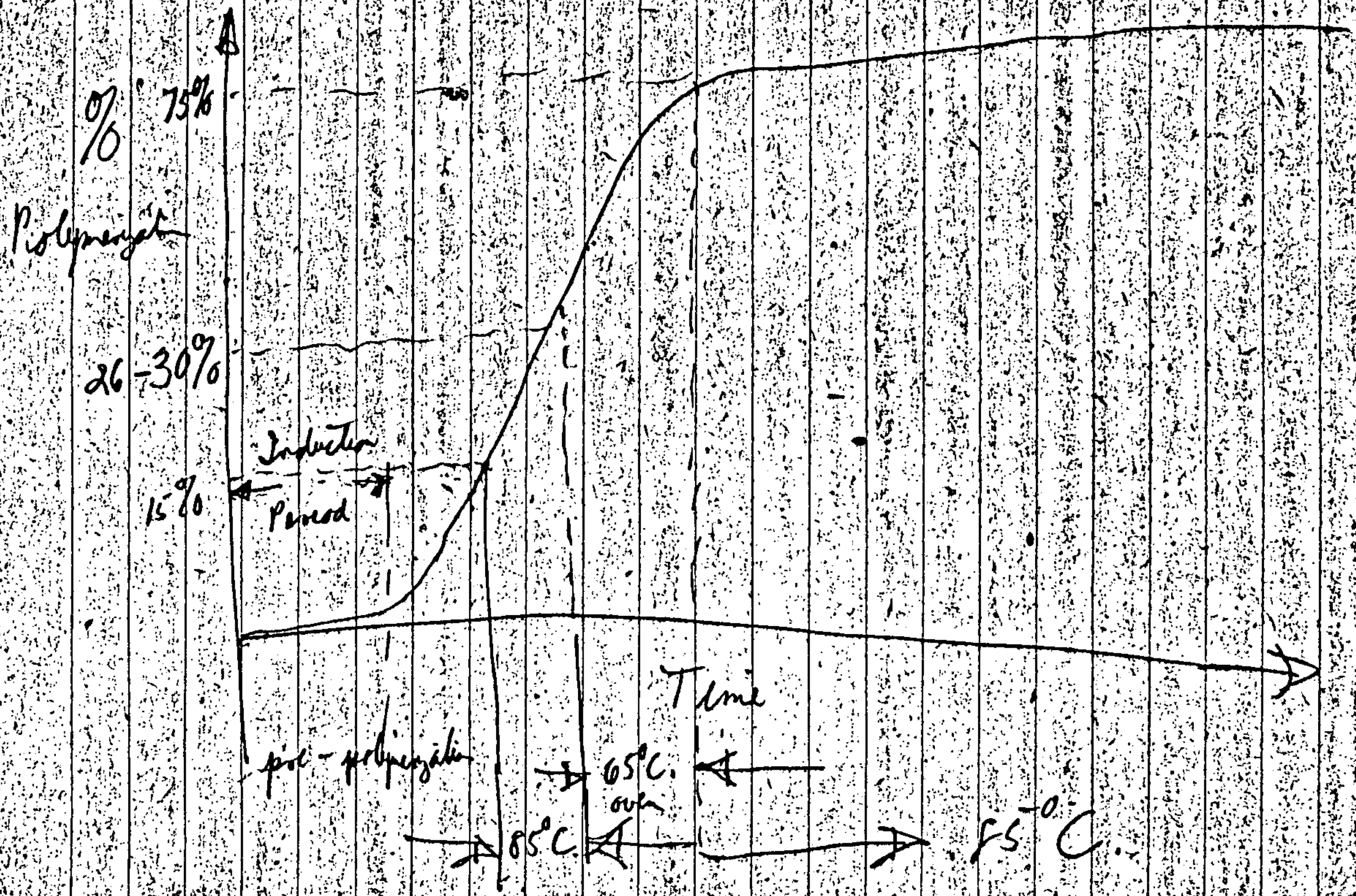
$$R'^{+} + R'^{+} \longrightarrow R'-R'$$

$$R'COO + H^{+} \longrightarrow R'COOH$$

$$R\overset{O}{\overset{\|}{C}}O\overset{O}{\overset{\|}{O}}R \rightleftarrows [RCOO]$$

$$RCOO \longrightarrow \underset{\downarrow}{\boxed{R^{+}}} + CO_2$$

#25


% Polymerization
75%
26-30%
15%
Induction Period
Time
pre-polymerization
65°C. oven
85°C
85°C.

#26

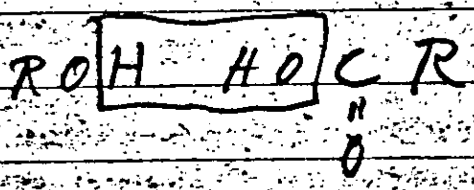
$NaOH \rightarrow Na^+ + OH^-$

$ROH + OH^- \rightarrow RO^- + HOH$

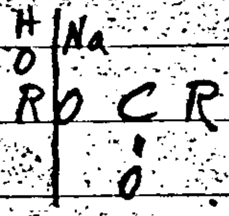
$RO^- + Na^+ \rightarrow RONa$

$RONa + Cl_2 \rightarrow NaCl + ROCl$

$ROCl + \frac{1}{2}Ca(OH)_2 \rightarrow ROH + \frac{1}{2}Ca(OCl)_2$



$RO\boxed{H\ \ HO}\underset{\overset{\|}{O}}{C}R$



$\overset{\overset{H}{O}}{R}\,\Big|\,\overset{Na}{O}\underset{\overset{|}{O}}{C}R$

$Cl_2 + NaOH + \overset{ROH}{\cancel{NaOH}} \rightarrow \overset{R}{\cancel{Na}}OCl + NaCl$

#27

Specification of valves not yet ordered.
Specification of Probe levels
Instrument layout + board
Electrical layout, space arrang't
H_2S system instrumentation
Design of Furnace.
Hastelloy B reactors not based on calculation.
Stanton was not told of abandonment of
these reactors.

Promised to call Gottlieb to change terms.
Promised letter of explanation from London.
Said I will be called to sign Monday
Was never consulted on Norman deal, except
for two instances of curt and evasive post
facto information.
Was not consulted on "cooperative".
Was not consulted on Klein-Levy Note
Was not consulted on dissolution 1947 August

#28

coinciding with the closing
the [illegible] a deal.

ear Ave;

Everything that we told you about the very precarious state of the Stanton job is exactly as we said it. It is most essential that you return in a ~~reasonable~~ [illegible] the shortest ~~[illegible]~~ so that the job can be properly concluded.

Further, we ~~believe~~ say that it would be ~~extremely~~ impossible ~~[illegible]~~ to ~~demonstrate (personally before and [illegible] a [illegible] [illegible] output)~~ ~~[illegible] a [illegible]~~ develop a modification of the cyanide process in a few days so that you could demonstrate it in Switzerland.

However! ~~If~~ you deem it proper to ~~[illegible] [illegible] 10 days~~ extend your stay so that you put in ~~[illegible]~~ ten days in London with the objectives of

1. Selling the diesel process to I.C.I.
2. ~~[illegible]~~ Selling the urea-formaldehyde glue to Wolfson

then please go ahead & do so. We will ~~[illegible]~~ try to keep Stanton ~~[illegible]~~ mollified here.

Harry & Phil

#.29

Dear Abe;

Everything that we told you about the precarious state of the

*the case

[illegible] impossible to develop evidence of

[illegible] process.

[illegible] for that

Ge 8 - 4823

#30

come back & finish Stanton deal so we can eat! (-)

No more than 10 da

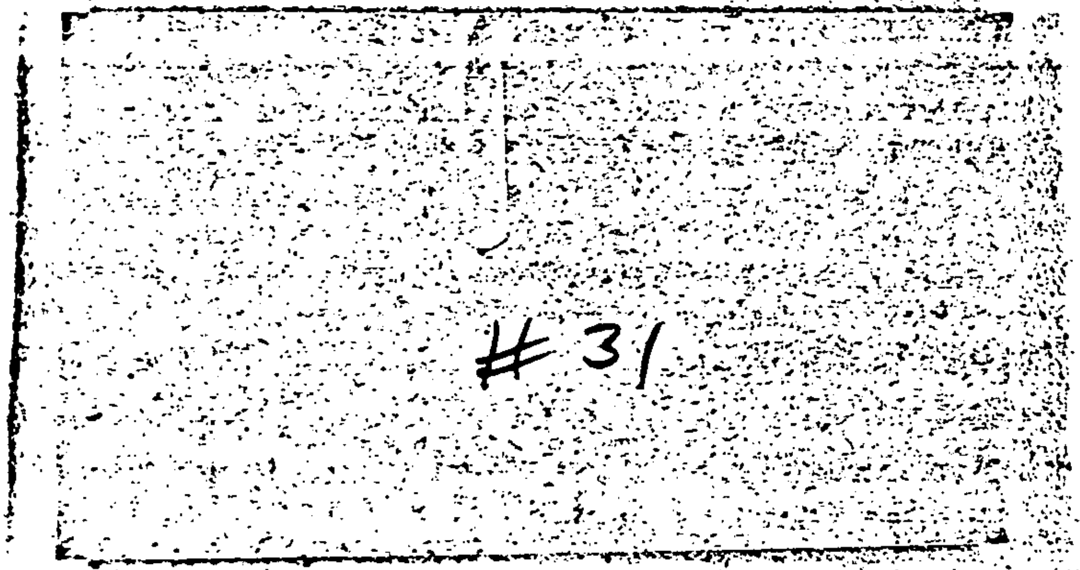
S

next week

over the phone

Release

Contras



#31

Tue
Thu
Fri
Sat

6 45 AM

Follow

Last Time

Health Doctor at [illegible]

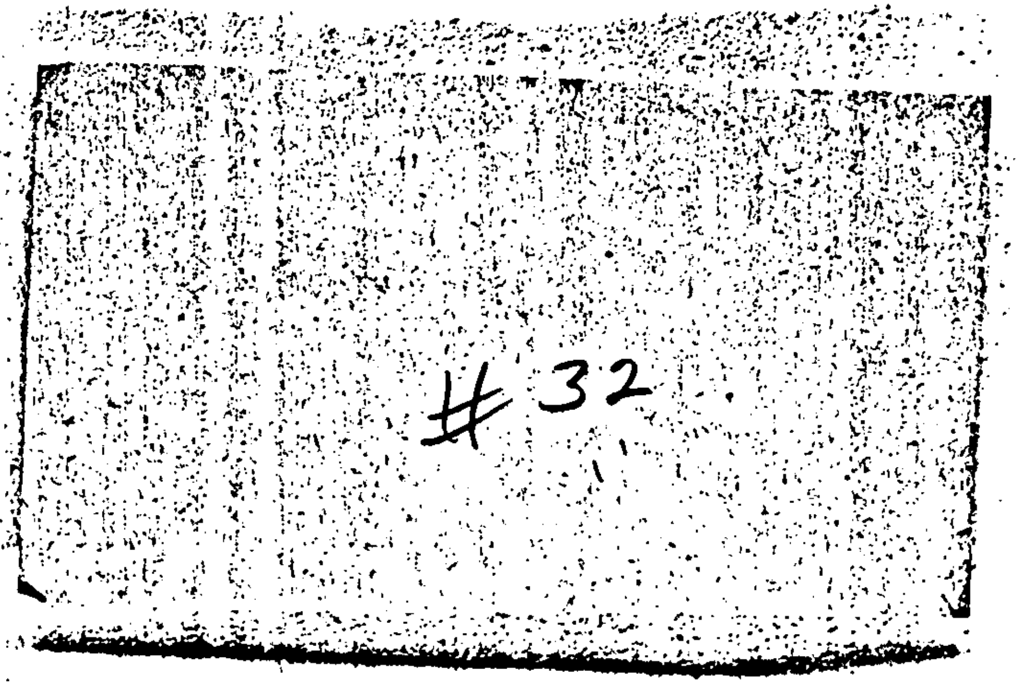
[illegible] Clinic

Ch(n ali

Campaign to

Campaign to Divide

1/6/50



#32

Campaign of Definite Pattern of Deception
(conscious or Unconscious)

A. Stanton

1. Lies on completion of job
   - a. End of Jan for design & drwgs — not <u>started</u> till middle of Feb
   - b. Telling Stanton we had made many runs in D.T. reactor and that we would give him yields, quality data etc. Evidence — letter. This we did not find out till we saw Stanton's request for the data.
   - c. H_2S Generators — Stories are told
     - (1) Could be purchased standard
     - (2) We had designed them before
     - (3) Complete negligence to consider the problem.
   - d - <u>Offering</u> to build a plant for Burma when the contract (Stanton) specifically forbids the sale or disclosure of such information. Evidence - Contracts and then telling Mike & Harry that the Stanton contract did not prevent him from signing with anyone else in the U.S.
   - e. Manifold promises to Stanton re completion of various items — See [illegible]

2. Oscar – The partner [illegible] [illegible] a [illegible]. If the man was (– partner in a field) had been told what was going on he

a- Norman Deal { never talked [illegible] / wanted [illegible] to [illegible] / we must tell [illegible] story

b- Dissolution of Partnership – [illegible]!

c. Larry's Judgement Notes

If not then he should have been released from the partnership arrangement and been kept on as a paid employee.

This man worked for four years (you took him away from his accustomed field) & now has nothing to show for it but a mound of debts + $7000 in salaries. This man has believed in you & stuck up for you – when Phil was dubious about coming here Oscar assured him that you were of the highest moral fiber; Oscar alone in 1948 had faith in your completion of the [illegible] polymerization. To replace Oscar you would have needed three men & you know it.

Left job which at least paid a salary

3. Phil – Came here & worked for nine months without pay – rec'd $600 & you [illegible] that much. Would tend [illegible] was on call at all & any hours to the extent of wrecking any privacy that he had and now [illegible]

salary is to be waived. as a [illegible]
cut in two cut (— "increase" (—) [illegible] but [illegible]
ask for a threat to strike) to 125 and the
150 we had provided & only in consultation
of practically every deal in Curios not only
the Company & only after 6 mos. is it to be
considered: The waiving of salaries had been
brought up but Phil had not agreed to
anything & you had said that we would
discuss it further with some rough
statement as to having a share in the
Co. Then in Childs Fri with you pulled
the 150 per week gag plus the info that
we would be making more money than you
& you would be borrowing money from us.
check Abe's statements re Budget

125 now for Abe — any evidence of fraud (i.e. not salary) & not
150 monthly — 115 — would have gone along.

Phil Harry Bill or [illegible].

never were we ever consulted on anything
Monday's crack about no going out to the
lot where we belonged only reflected what
you thought

21. Harry — Have worked avg of 80 hrs/week
since have been with ABA. Cuts & Curios
always in at 9:10
before that Oct. always on call. Have stuck

[illegible]

[illegible] back to extent of 1000 to people [illegible] [illegible]. Have kept every promise ever made to abe. All protestations as to Harry working two [illegible] were just for public consumption — never any intended to ask (and just took for granted) that they work any & all hours under the pressure of various continuing states of emergency (Powers, [illegible], [illegible], Eddie Q, Mody, [illegible] etc, etc. — much before my mother died.

However as lately I refused you would put on your [illegible] act of not saying anything (said [illegible] Switzerland, Z[illegible], etc.).

Promises

a. [illegible] that we would be pd back salaries + bonus (idea advanced by Norman for our sticking by G.) — [illegible] gullible. agreeable dope like H. to agree to [illegible] salary at [illegible] after a [illegible] of talk

Know that I was anxious to get back to Phila & knew that I wasn't [illegible] was [illegible] — so I wouldn't even be around for my [illegible]

All talk of stock distribution baloney — look at Norman contract & [illegible] plus, most important, are knowing full well that Harry would not [illegible]. But [illegible] off with [illegible] answer.

a. [illegible] — [illegible]
for him again — taking one of fantastic
project for completion in [illegible] short
time.

(1) Polyvinyl Cl — Polyvinyl Acetate
(2) Lonza — [illegible] → Mc Ne [illegible]
(3) H.T.H. — [illegible]

would ever have any time for myself. In
two years have never been able to see my
cousins even once. All talk about my
having no social life is just brushed [illegible].

Hard worker.
J. Bill — Loyal as all get out. Quiet. Need
say no more. Bill apparently was not even
asked about increase of salary.

6. Bernie — Been friend. Lent money without [illegible]
interest.

Campaign to Discredit (beautifully staged up by [illegible])
1. Bernie — complaining. True enough. But pointed up
other faults — small. You expect tolerance for
your many small failings ([illegible], [illegible]
up other peoples [illegible]) so why not do so for
him.

✓ Phil — [illegible] other chemists work. True but
again pointed up. Vs. Phil's other qualities. Telling
Harry he's another Weber.

3. [illegible] - [illegible]
too much (about wanting to go home). also that I was not as good a chemist as [illegible] had at first supposed.

4. Duane - Shylock. Was just hanging around for something good. [illegible]'s vicious attacks & you right there. [illegible] got [illegible] of you then

5. Ike, Bob - revisions & vilification
only [illegible] was Coop. a screwed up affair if ever there was one.
which [illegible] did. But [illegible] couldn't attack him because he had made criticisms which [illegible] of selling promises before we had them & out of book.

II Gen'l

1. I & Big Deal Delusions
a. after promises to me on starting job.
b. We are only small cog a [illegible] [illegible] - which so much. Should realize that the cards are stacked against us.

2. Selling promises before we have them - Very bad business which drives us to do work hastily, poorly, & without proper looking up
a. M-M
b. H.T.H.
c. Polivinyl Cl - A2O [illegible]

whole demonstration in [illegible] in view of
957, [illegible] ([illegible] from date)

3. our protests against Dealing with [illegible] till
[illegible] + within + your deputies of them.
[illegible] [illegible] obvious [illegible] goodwill.

II - Suggestions for Future
1. Finish Stanton job
2. Operate on a much reduced scale. Have
Naomi [illegible]. [illegible] + [illegible] [illegible] [illegible].
3. If [illegible] Dial to O.C.I. [illegible].

I - Immaturity
1. Deliberate campaign to wreck your home
life.
2. Deliberate campaign to leave only a Northern —
minority controlled org. Reason for opposition to Norman.
3. Greed - you said yourself that the 2 [illegible]
money.
4. Has fought with everyone [our family / everyone with whom AMA] & is absolutely incapable of getting along with anyone —

(Time limit)
and return (are his word) on all [illegible] ~~to~~ Stanton
dead.

$7,000
2m
$2,500

~~madness~~
irritation
1. ~~[illegible]~~ To complete ~~one~~ [illegible] by only dues
so that - you

(haven't heard from [illegible]

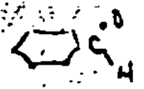
---

1. Conditions in which left Cy.
left us without money to run office - rent etc
no money for living expenses
~~phone~~ telephone about off Tomorrow
most important - Stanton
2
very shocked [illegible] because he wasn't
back already
~~[illegible]~~ Entity that mystery 18,000
sit, threat, to break contract for which
in two [illegible] grounds

3. Faced with having a
all Wolfson &
for will take too long for him to demonstrate
~~[illegible]~~ What are you going to do?"
Judging from his letter he would stay
longer than a

#33

To Be Done

1. ~~Run Battlemann for [illegible]~~
2. Chlorinate 
3. React Cl prod of 
4. oxidize 
5. Try to rep HCO3 by OH in HSO4 
6. Prep map samples in V. C. (also [illegible])
7. Set "Trap" in V. C. ([illegible])
8. Prep "Quick Vision" in V. C.
9. Get V. C. samples [illegible] (after "6")
10. ~~[illegible]~~
11. Carry out solvent tests
12. arrange samples [illegible], Writes for C. Q.
13.

Petrolite
BO 9-9088

500
1035
700 } Called for samples
Nov 10 '47

30 Broad St.
near Bdwy & New St.

Wed morning

Amcon Corp.
29 Bdwy
N.Y. 6, N.Y.
BD 9-2668

Call Wed. morning
Mr. Turner

(55)

5 Call
5 Conf Call
10 Home [illegible]
5 AM Confine

(25)
(15) week

Chem. $\overset{\text{Nov 16}}{\text{Z.tg}}$ 49

779-91 (1925)

H. Decker

KH [illegible] [illegible]

Am. 47, 3159

KOH in [illegible] V 464

nil ~~464~~

Water 180-200°C

~4 hr.

NaOH + MeOH

Agfa DRP 411,050

→ amine & phenol

nil V2 p. 160

Beil $\overline{V}$ 200

Cl 

Vandevelde
C. 1898 I 438
~~no~~ Cl splitting
long cooking

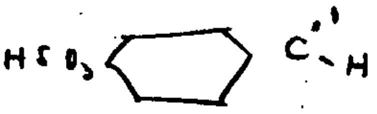
6 hr cook with KOH
not changed
Fittig Ann. 133, 49

Br  V 208

Boiled down 4 with KOH
water or alc.

Riche C. r. 53 588
Ann 124 359

① 10-28-47



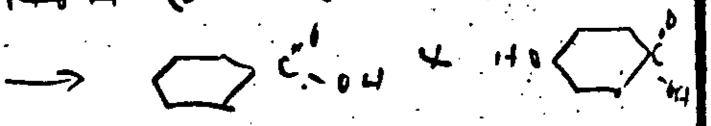
Beil. 11, 325

Prep.

pass HSO3  CH3 into a mixt of 25% oleum & MnO2 (D.R.P. 154,528, C. 1904 II, 1269).

React.

Heating with KOH & H2O @ 220-240°C



Ber. 12, 2511

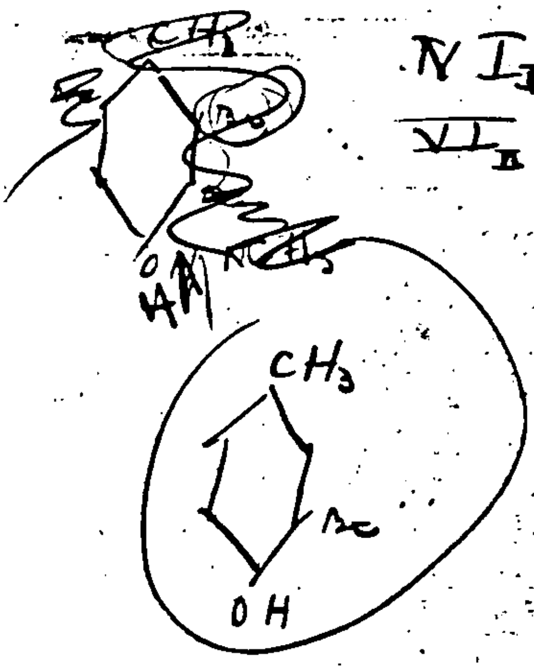
Na salt - needles.

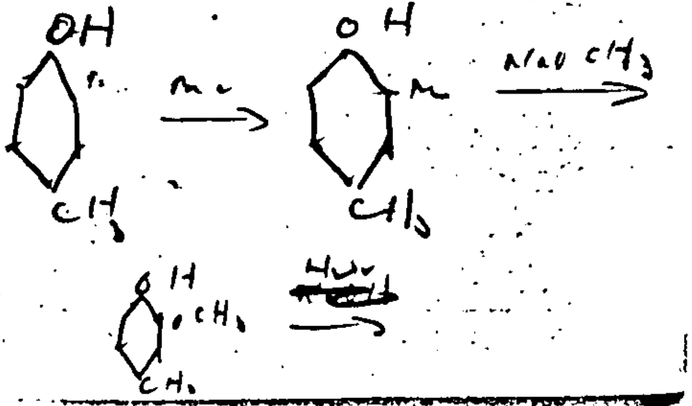
②

[redacted]

IV I_{II} uiy

VI I_{II} vor





col. liq.
b.p. 218-219°C
m.p. 57-58 °C
(needles).

Beil - 6, 405

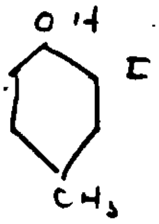
2-Brom-p-Kresol.

orig-art.

Liebig's Ann. 320, 203
(1902)

T. Zincke & K. Wiederhold

Prep
1. Diss OH cpd in 5-6 times
quant of $CHCl_3$.
2. Cool [illegible]
3. [illegible] [illegible] [illegible] Br_2
4. Let stand for 2 days
5. Distill → [illegible]
6. [illegible] [illegible] [illegible] pet ether.



m.p. 35°C

b.p.12mm = 117°

Beil 6, 411

Ber. 17, 2533
Schall u. Dralle.

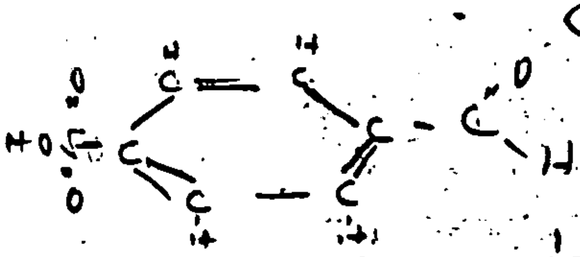
p-OH-cresol → Na salt (dry)

→ conc with CS_2 →

pass in I_2 → keep

refluxing

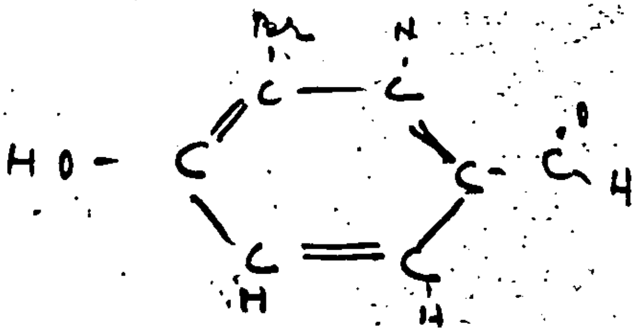
(7 D)



11 3-5

Formal negative

$C_7H_6O_4S$



$C_7H_5O_2Br$ (Cl, I)

Formal negative 2-4

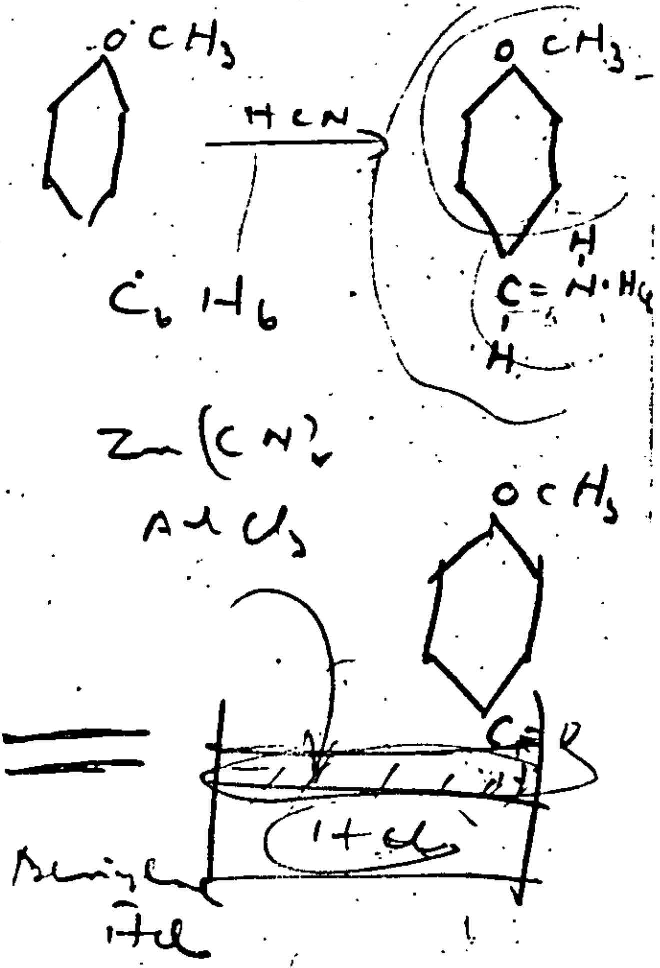
8, 54

8, 63

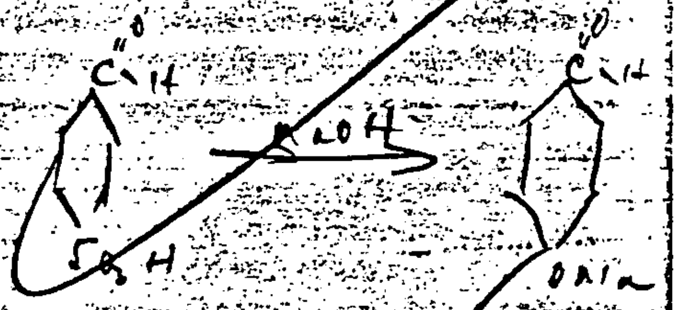
3Br, 4-OH 8, 82 (5, 3Y)

8, 81

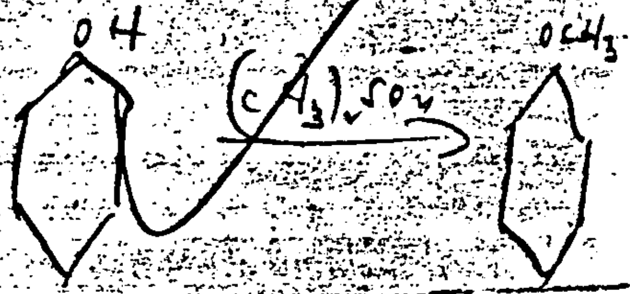
3-Cl, 4-OH benzaldehyde


OCH3
HCN
C6H6
OCH3
H
C=NH·HCl
H
Zn(CN)2
AlCl3
OCH3
C=O
HCl
Benzene
HCl

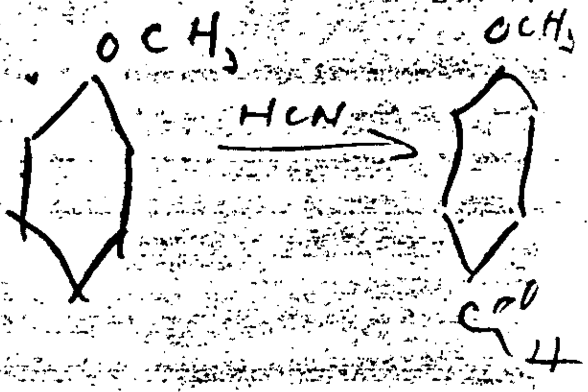
Method I



Method II

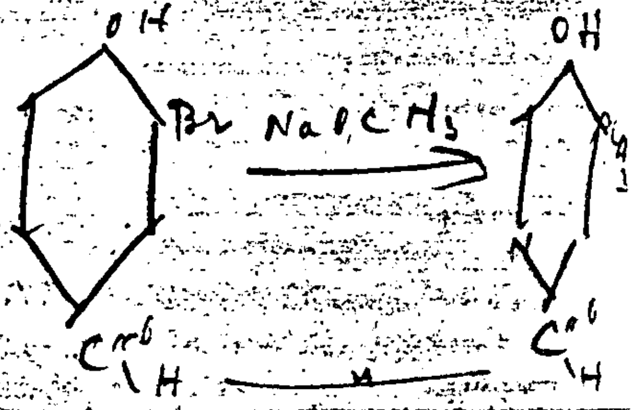


Sched III



Sched IV

atoms of pres.



dee
6/6/50

$$\frac{3.9 \; 1.7}{5.6}$$

$$\frac{4.9}{5.6} \times 50 =$$

44.9.

$$\frac{4.9}{} \qquad \frac{4.9}{1.94} \times 9.2$$

2.3

4.6

C_6H_5OH

72
6
16
94

[illegible] [illegible] [illegible] get
out away fast.

Const.

less than 0.6 m.f.s.
650-950 ft²

10 [illegible] immediately
[illegible] 40,000 ft²

Improvements
1. [illegible] of [illegible] yrs
good 3.5% [illegible]
[illegible] [illegible]
Higher [illegible]

2. Work [illegible] → diff.
districts of [illegible]

1. F-T not competitive with Nat. Prods.

2. CO + H → C₁ [illegible] H-C
(+ alc., aldos.)

3. Use Fe, [illegible]
170–270° Ni + Co.

4. [illegible]
170–270 / [illegible]
[illegible]

5. Pressure
Ni not above 1 atm.
[illegible]
Co 10–25 atm.
Fe 50 atm.
Ru 1000 atm.
(only [illegible] 1100 atm.)

3. Can get as hi as 45-20
gasoline & lower wax
content (by varying
catalysts) -
~ Fe

Germans used Fe not
because it was cheap but
because
a. Co was not available
b. Fe more versatile
(actual so) -

4. Recycle process
Push gas thru so fast
that it carries out heat as
sensible heat 100 ~~fresh~~ recycle
gas to 1 fresh gas.
(Michael)

44% Gasoline 20 oct

11% D.O. ~~[illegible]~~ 160-70 al

7% alcohol etc H
in to C_5

7% C_4 H-C

3% C_3

5% $H_2C=CH_2$

7% wax

5. Liq Phase Process
Suspend cat in liq. &
bubble thru gas.

c. 300 - 320 °C

d. [illegible]

e. $2 H_2$ to 1 CO

f. ~~[illegible]~~ [illegible] was but [illegible]
[illegible] catalyst

g. Set C formation —
unpredictable of bed
(may get [illegible]

h. Keep p.p. of H_2 high to
reduce C formation.

i. $2CO \xrightarrow{+H_2} \underline{C} + H_2O$

Carbide → C - C
[illegible]

6 use oil cooling

---

7. use mostly ppt'd cat.
↳ ~~[illegible]~~ of Co.

Fe (+ Cu + Zn)

U.S.

1. use fluidized technique.

2. Diffs
   a. Use contact heat exchanger
   b. "Water design"
   c. Particle size - Dim -
      linear Vel. etc
3. Use NH_3 type cat.
   a. Not thoroughly
   b. [illegible] [illegible] v = 5 microns dia
      v [illegible] dia

Ru [illegible] much more durable
at 100 atm than any
other cats.

10. at hi Press
a. get more hi MW prods.
b. Ru at 100 atm →
waxes of M.W. 10 - 25,000

11. Use mixed cat in
most work.

---

12. Co cat. [illegible] 100°C
more + C+ chain
in Hexane etc

Fe cat C_2 [illegible]
apparently in Hexane

Synol.
~~Synthol~~ Process

1. Prodn of alcs & mixtures
of olefins & paraffs.
Diff condns.
2. use fused NH3 type cat.
3. use 190-200°C
20 atm
use hi recycling tail gases
use hi linear vel
4. If use 210°C or not
hi linear vel. get only
10% alcs.

probably alcs are
precursors of olefins

alcs exclusively st
chain N alcs.

need more work on
cat durability — at 1
[illegible]

6. all cats give detectable amts of carbonyls.

7. also get carbides.

Fe large amts

Co. small amts

Ru none.

at 70% Co C then have inactive cat.

so treat with H_2 and CO.

for Fe 100% Fe_2C get active catalyst.

8. Temp coeffs:

1.6 & 1.8 for Co & Ni

& lower for Fe

8. Press coeff.

p_{CO}

zero for CO in absence of prods. but removal prods quickly is at l. coeff of ½.

Ru. press coeff is 1 in operating range

Ni coeff = ·7 at 300°C

9. Cat durability greater for > press

Co at low pressures get fouling of cat by hi boil paraff waxes

5 atm best.

Result is worse for Fe.

65-4307-1-0-13(C3)

[illegible] 14

SAC, Philadelphia

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

7/10/50

EXHIBIT 65-4307-1B-13 (3) (Exhibit 14)

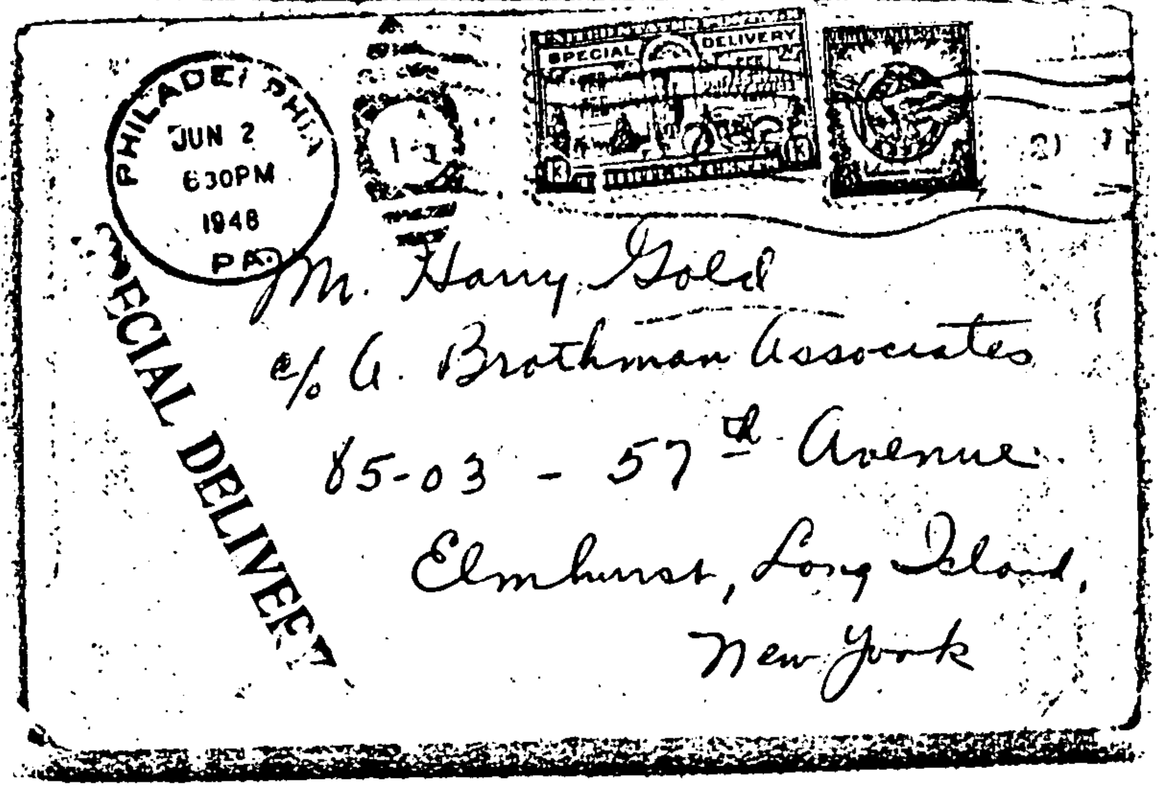
On 6/22/50, GOLD advised that this was a letter from his friend, MORRELL E. DOUGHERTY, in which DOUGHERTY must have sent GOLD about $5.00, as this was the time that GOLD was without funds (June 1948).

TSM:HKF
65-4307

Harry -

Hope you
get this in time
See you soon.

Doc



PHILADELPHIA
JUN 2
6:30PM
1948
PA

SPECIAL DELIVERY

Mr. Harry Gold
c/o A. Brothman Associates
85-03 - 57th Avenue
Elmhurst, Long Island,
New York

Morell E. Dougherty
5517 Litchfield St.
Phila. 43 Pa.

FLUSHING, N.Y.
JUN
8
3 AM
1948

6-6-50
Ack

65-4307
Ex 15

SAC, Philadelphia 7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (4) (Exhibit 15)

On 6/22/50, GOLD examined this notebook and stated that it could be in the handwriting of SHOLEM "SY" SILVERSTEIN. GOLD stated, however, that there are certain pencil notations in this notebook which are in the handwriting of GOLD himself and pertain to work while the latter was employed at A. BROTHMAN AND ASSOCIATES.

The loose papers in the notebook are in the handwriting of GOLD and BILL ROBOLL and are concerned with an experiment in trying to make methyl methacrylate molding powder.

TSM:HKP
65-4307

Pat. Jan. 28, 1941. App. Mar. 2, 1940

2,229,897 — for synthesis of α-OH isobutyric acid, — American Cyanamid Co

[I] Heating with mineral acid tends to decompose the cyanhydrin, therefore the cyanhydrin is first taken to the amide stage, then the temp. is raised for the completion of the hydrolysis.

[II] Example =

(A) 100 parts of acetone cyanhydrin are placed in a water-cooled vessel + 132 parts of concentrated HCl are added under agitation at such a rate, that the reaction temp. does not go over 30°. Continue cooling if necessary to keep temp. below 30°.

(B) After about 4 hrs, there is a 99% conversion to the amide. (After 12 hrs. practically quantitative.)

The solution of the amide is heated for 4 hrs. at 90°C, & quantitative conversion to the α-hydroxy iso butyric acid is obtained.

Ⓒ Neutralize with NH_3 & filter off ~~crude~~ NH_4Cl.

Ⓓ Evaporate the solution under vacuum to obtain crude acid.

Ⓔ Purify by crystallization from benzene or or distillation under high vacuum.

6/2/50

Jan. 23, 194

α-hydroxyisobutyric acid

Purpose -- test run hydrolyzing acetone cyanhydrin to α-hydroxyisobutyric acid

Procedure (per U.S.P. 2,229,897)

[I] Quantities -

For this run a pound of acid = 454 gms is wanted - The mol. wt. of the acid is 104 gms/mol; mol wt cyanhydrin = 85 gms/mol

$\frac{454}{104}$ = 2.29 gm mols/lb of acid

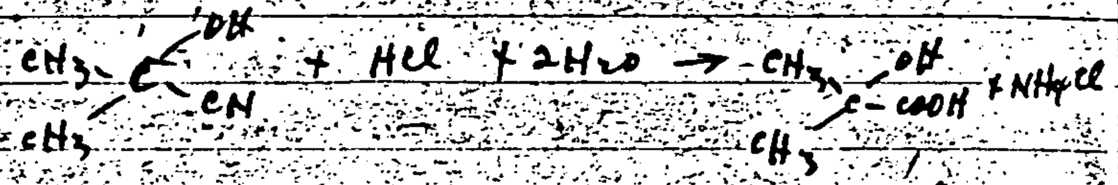
(A) cyanhydrin required - assuming a 50% yield

$2.29 \times 85 \times 2 = 390$ gms.

$\frac{390 \text{ gms.}}{0.932 \text{ gm/ml}}$ = 420 mls. cyanhydrin for 1 lb. α-OH isobutyric acid

Ⓑ

Requirements of HCl



$$CH_3(CH_3)C(OH)CN + HCl + 2H_2O \rightarrow CH_3(CH_3)C(OH)-COOH + NH_4Cl$$

Since 4.58 mols of cyanhydrin are required, 4.58 mols of con. HCl are needed.

$$\frac{4.58 \text{ mols con. HCl}}{12 \text{ mols con HCl/liter}} \times 1000 = 382 \text{ mls con HCl}$$

theoretically required

However the patent calls for 132 parts con. HCl for 100 parts of cyanhydrin:–

100 gms. cyanhydrin = 1.18 mols cyanhydrin

0.85

D.C

132 gms. HCl

1.19 gms/ml × 12 mols HCl = 1.33 mols HCl

1000 mls.

2/6/50

1.33

1.18

1425

5.17

1.2

cyan

con. HC

6/6/50

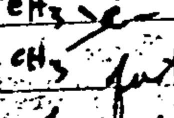
1-24-47

II Operations 1

9^50 - start adding HCl - temp. 15°

10^18 - complete addition - temp. held at 25-26° during most of addition up to 31° for short period

10^18 - 1^40 - clear reaction mix has a light yellow color; reaction proceeded since temp. rise occurred unless cooling was maintained temp. range - 23° - 27°

1^40 - solution became turbid - presumably  $(CH_3)_2C(OH)-CONH_2$ has precipitated out; no further temp. rise noted & no odor of HCN, only HCl & another organic odor - probably amide

2^20 - Start heating, at 50° the solution clears; becomes cloudy again at about 70°

Δ 2^35 - up to 105°; lowered to 93° & maintained in range 90°-93° -

Note: a heavy white ppt. has formed

6^15 - St

hea

from

6^35 -

of NH_3 added

7^20

6^{15} – stop reaction, cool – ~~solution~~ slurry has developed light green color, possibly from stirrer

6^{35} – down to 22° – start neutralizing with NH_3 – cool while neutralizing – NH_3 required = 520 mls. – Huge volume of NH_3 needed may be due to buffer action –

7^{30} – neutralization complete

1-27-47

α-OH-isobutyric acid

Purpose - obtain α-hydroxy isobutyric acid by hydrolysing acetone cyanhydrin

Procedure -

$\boxed{\text{I}}$ - Quantities

(4.58 mols)
acetone cyanhydrin — 390 gms. - 420 mls.
conc. HCl — 514 " - 432 mls.
(5.17 mols)

$\boxed{\text{II}}$ Operations

12^{15} - started adding HCl to cyanhydrin maintaining temp. at about 25° - all added in about 25 minutes

3^{10} - first turbidity visible, & few minutes later heavy ppt. in liquid is present - presumably the amide

4^{40} - started heating

4^{50} - 90° - up to 105° for few minutes
cooled rapidly

1-28-47

α-hydroxyisobutyric acid

Purpose - Synthesis of α-hydroxyisobutyric acid from acetone cyanohydrin

Procedure:-

$\boxed{I}$ Quantities:

acetone cyanohydrin — 390 gms - 420 mls (4.58 mols)
conc. HCl — 514 gms - 432 mls (5.17 mols)

$\boxed{II}$ Operations -

1^{25} - start adding HCl - temp. went over 30° to about 34° briefly - all added in ½ hr.
4^{45} - amide begins to precipitate
5:30 90° bath introduced, reactants clear when at 55°C. Ppt. again at 79°C.

1-29-47

α-hydroxy isobutyric acid

Purpose - Synthesis of α-OH isobutyric acid from acetone cyanhydrin - using double previous quantities

Procedure -

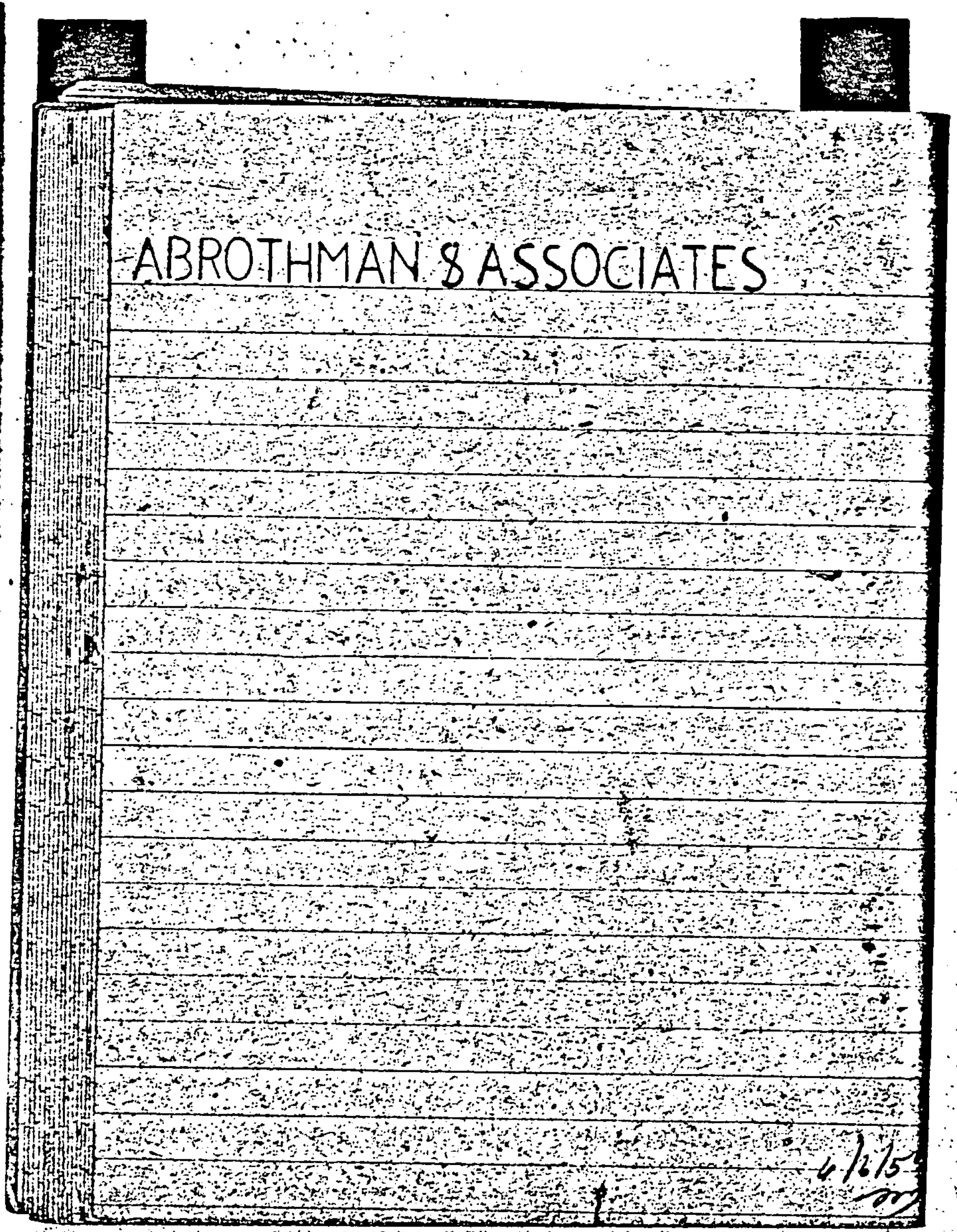
$\boxed{I}$ Quantities -

acetone cyanhydrin - 780 gms } 9.16 mols
$\boxed{840 \text{ mls.}}$

con. HCl - 514 gms. } 10.35 mols
$\boxed{864 \text{ mls.}}$

$\boxed{II}$ Operations

10^{50} - start adding HCl
11^{30} - all added
2^{00} - reaction mix turbid due to ppt. amide
3^{40} - start heating to 90°
3^{55} - to 96° - cool



ABROTHMAN & ASSOCIATES

4/12/5

1-30-47

α-hydroxy isobutyric acid

Purpose - Synthesis of α-OH isobutyric acid from acetone cyanhydrin

Procedure -

$\boxed{I}$ Quantities -

cyanhydrin - 780 gms. - 840 mls. } 9.16 mols
con. HCl - 514 gms. - 864 mls. } [illegible].35 mols

$\boxed{II}$ Operations
11^{35} - start adding acid
12^{10} - acid all in
2^{15} - ppt. appears.
4^{15} - cool to about 10° - 12°
& let stand overnight with agitation.

1/31/47 [Note - ppt. did not dissolve on heating to 90°]

10^{25} - start heating
10^{45} - reached 90°

2^{55} - remove bottle

Since there is an excess of 1.19 mols of HCl, 1.19 mols NH_3 will be needed to neutralize -

$$\frac{1.19 \text{ mols}}{14 \text{ mols/liter}} \times 1000 = 85 \text{ mls. conc.}$$

3^{35} - 85 mls. NH_3 added with cooling

3^{45} - filter - filtrate has deeper orange color than previous time

6/6/5

6/6 13

2-4-47 - Dehydration of Ester

Purpose: attempt to dehydrate methyl α-O isobutyrate assumed obtained ~~in~~ previously with finely powdered silica gel.

Procedure -

[I] Quantities

60 gms. of ester
75 gms. of silica gel

[II] Operations

(A) refluxed for about 7 hours — The temp. of the vapor was close to 65° C after 2 hrs. of reflux, and the mix temp. was about 77°C.

The reflux did not take place gently b in ~~spurts~~ bumps. There was no stron odor of HCl at exit end of conde but the flask had a very strong odor of HCl.

Ⓑ 2-5-47

Refluxed material was distilled:

flask temp.	bottom column	upper column	pressure
30°	32°	29.5°	94 mm
36	37	35.5	
34.5	34	29	

The distillation took only a short time, i.e. about 20 minutes. The indicated drop in temp., i.e. the last reading took place when most of the distilland had coming over, and the vapors were not sufficient to hold the thermometer to temp.

No appreciable column reflux, tho there was a residue of droplets on the column walls.

2/

Distillate — 26 gms.

Residue on walls of column — about 12

Taken over to the pump or retained

by silica gel — about 22 g

The distillate had an odor suggestive

methanol, the residue in the flask and on column walls had a strong HCl odor.

6/6/5

2-7-47 Esterification of α-OH-isobutyric acid

Purpose - Esterification of α-OH-isobutyric acid using reflux temperature, + passing in dry hydrogen chloride.

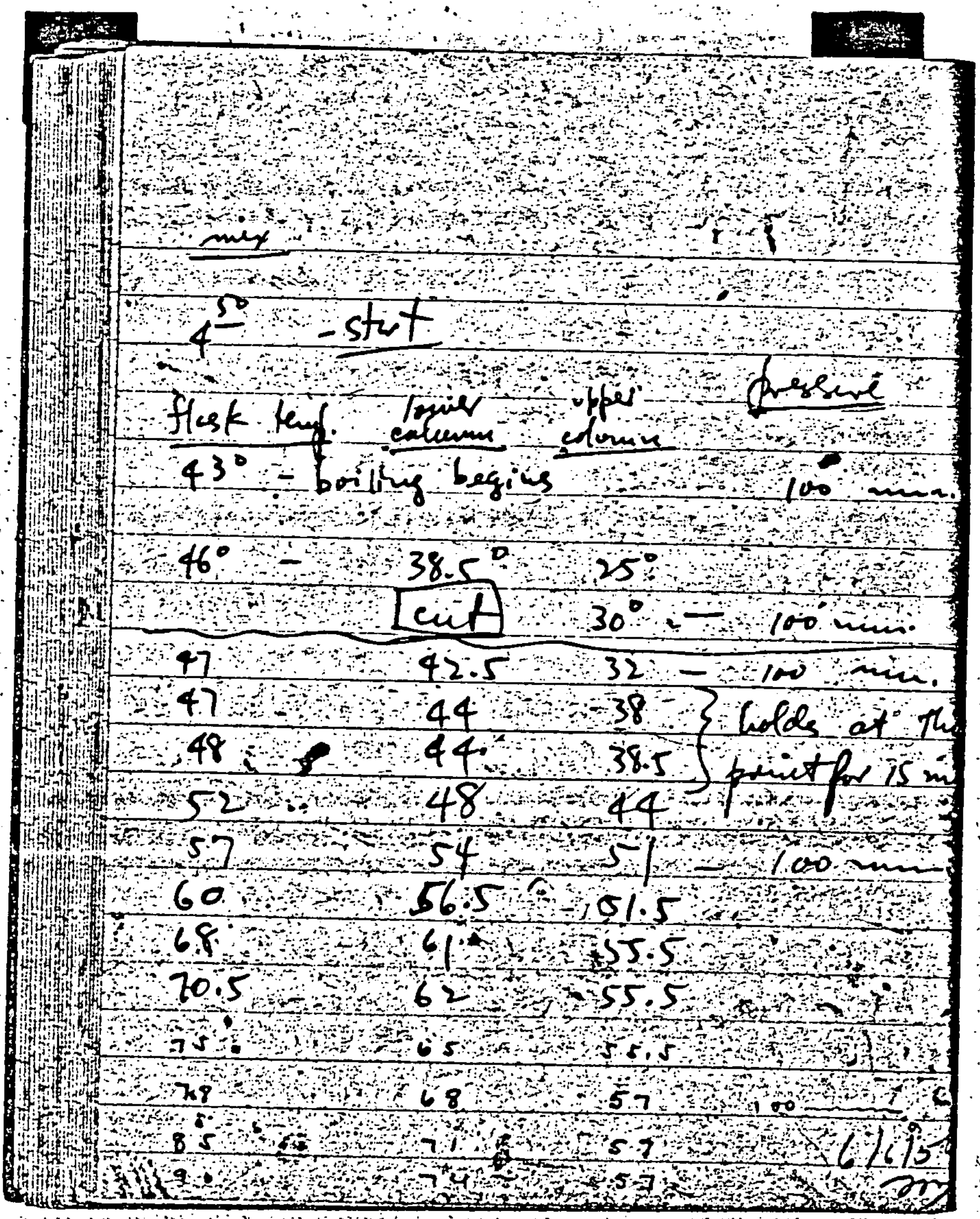
Procedure

I Quantities -

4 to 1 mol ratio MeOH to acid { 78 gms. α-OH-isobutyric acid - 0.75 mol
96 gms. methanol - 3.0 mole
100 gms. silica gel (finely powdered)

II Operations - Ⓐ Dry HCl bubbled in for 8 hrs. under reflux conditions

2-10-47 Ⓑ Distil (20 mls. MeOH added to wash fluid from filter flask to 3 neck flask). Some silica gel still in



mix

4^{50} – start

flask temp.	lower column	upper column	pressure
43° – boiling begins			100 mm.
46° –	38.5°	25°	
	cut	30° –	100 mm.
47	42.5	32 –	100 mm.
47	44	38	holds at th
48	44	38.5	point for 15 m
52	48	44	
57	54	51 –	100 mm
60	56.5	51.5	
68	61	55.5	
70.5	62	55.5	
75	65	55.5	
78	68	57	100
85	71	57	6/6/5
90	74	57	

Flask Temp. °C	Lower Col. °C	Upper Col. °C	Press.
	78	57	100 →
100	81	57	
110	92	57	
112			

Yield
289 flask + Tare
200 tare
89 gms

Residue
201.0 flask + Tare
172.0 tare
29.0 gms

2-11-47

Esterification of α-OH isobutyric acid

Purpose - try esterification of the acid with methanol by saturating a portion of the MeOH with dry hydrogen chloride + using anhydrous Na_2SO_4 to take up the water.

Procedure -

[I] Quantities -

4/1 mol ratio alcohol to acid {
52 gms. α-OH isobutyric acid — 0.5 mol
64 gms. methanol — 2 mols
[dried over $CaSO_4$]

15.1 gms. Na_2SO_4

[M.W. of Na_2SO_4 = 142. Considering $Na_2SO_4 \cdot 7H_2O$ formed and 0.5 mol of H_2O to be removed then 0.071 mols of anhydrous Na_2SO_4

will take up 0.5 mol of water = 10.08 gm
+ 50% excess - 5.04

$\boxed{15.12}$

II operations.

A 16 gms. of methanol were saturated with hydrogen chloride and added t balance of 48 gms. of methanol containing 52 gms. of ~~a~~ α-OH-isobutyric aci and 15.1 gms. Na_2SO_4 - Stirred f about 5 hours. Then heat to 50° for 2 hours.

2-12-47 B Distillation at reduced pressure thru Vigreux column.

time	flask temp	lower column	upper column	[illegible]
2:25	26°	25.5		[illegible]
2:28	26	30	27	
	33.5	30	28	[illegible]
about 2:50 cut	33	30	27.5	

6/6/3

time	flask temp.	lower column	upper column	pressure	notes
3^{05}	38°	32°	37°	100mm.	
3^{15}	41°	35°	28°	"	
3^{20}	43.5	36	30	"	
3^{25}	43	34.5	28	"	
3^{30}	48	41	33.5	"	
3^{35}	52	45	35.5	"	
3^{45}	60.5	53	44.5	"	
4^{00}	67	57	42.5		} CUT
4^{15}	72	58	35		
					start heating
5^{45}			50	69-	
5^{55}	71.5	60	45	50	
5^{58}	72.5	60	45	50	
6^{05}	85	70	60	30	
6^{10}	83	75	59.5	30	
6^{15}	89.5	76	54.5	30	
6^{25}	98	85			cut

2-13-47

Esterification of α-OH isobutyric acid

Purpose - repeat esterification using using 1st fraction from distillation of previous run + portion of 2nd fraction to make up 64 gms. corresponding to 64 gms. of methanol used in previous run

Procedure -

$\boxed{I}$ Quantities -

"methanol" - 64 gms (as indicated above)
α-OH isobutyric acid - 52 "
Na_2SO_4 - 15.1 "

$\boxed{II}$ Operations

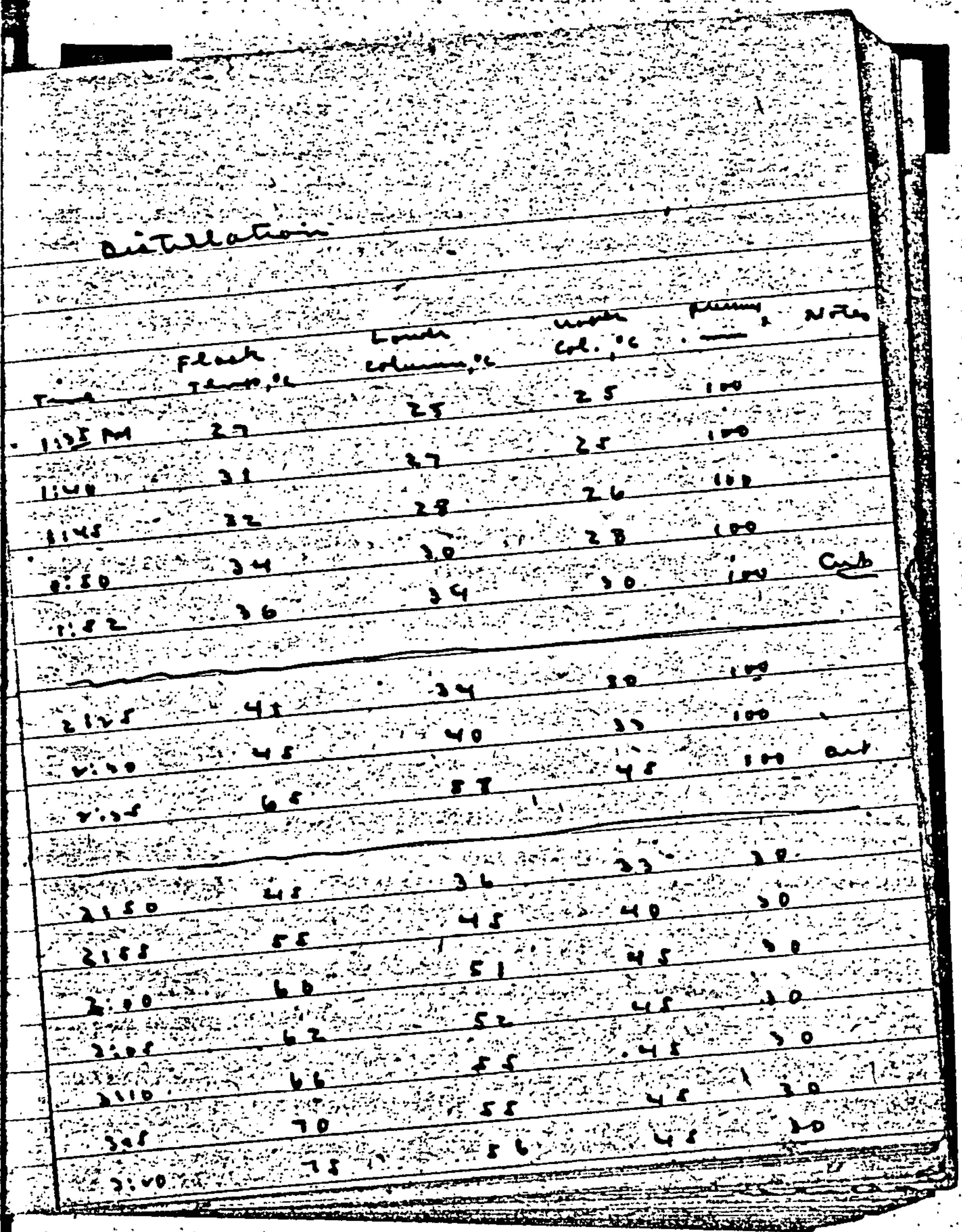
Ⓐ 16 gms. of "methanol" were saturated with HCl (heat of solution evident)

Ⓑ Reaction at room temp. of ~~tot~~ all constituents with stirring

start - $11^{\underline{40}}$
end $4^{\underline{40}}$ - p.m. start heating

ⓒ Heat for 2 hours with stirring at

6/6/5



Distillation

Time	Flask Temp,°C	Lower column,°C	Upper Col.,°C	[illegible] %	Notes
1:35 PM	27	25	25	100	
1:40	31	27	25	100	
1:45	32	28	26	100	
1:50	34	30	28	100	
1:52	36	34	30	100	Cut

2:25	41	34	30	100	
2:30	45	40	33	100	
2:35	65	57	45	100	out

2:50	45	36	33	30	
2:55	55	45	40	30	
3:00	60	51	45	30	
3:05	62	52	45	30	
3:10	66	55	45	30	
3:15	70	55	45	30	
3:20	75	56	45	30	

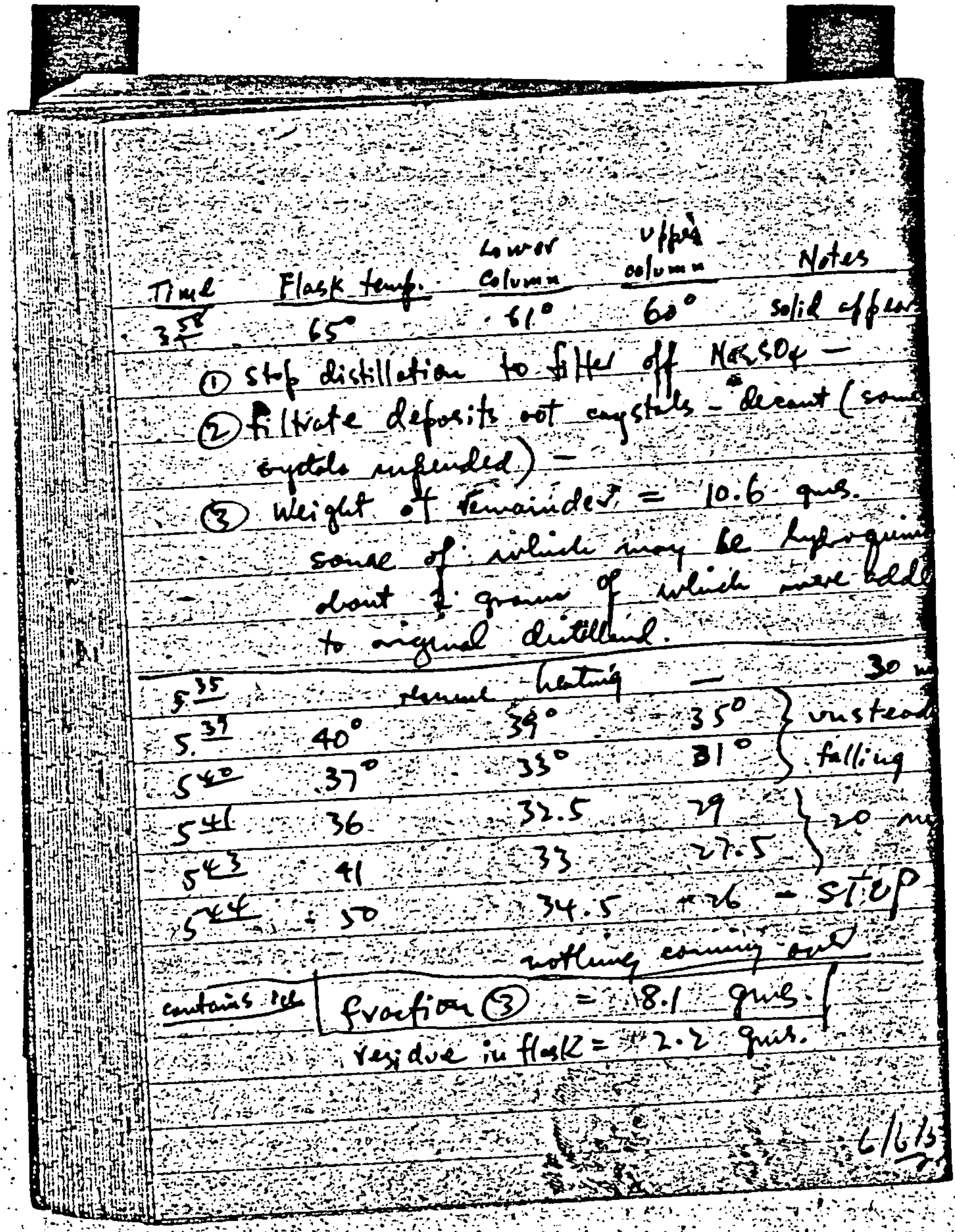
2-14-47

Distillation of Product of Vapor Phase Esterification — {weight of distilland = 231.7 gms}

Time	Flask Temp.	Bottom column	Upper column	Notes
1^{47}				start
1^{55}	29.5°	28°	26°	— rapid condensate stream
2^{00}	32	30.5	28.5	— 100 mm.
2^{10}	35	32.5	30	" " } CUT

wt. of fraction ① = 80.1 gms.

Time	Flask Temp.	Bottom column	Upper column	Notes
2^{25}				resume distillation
2^{40}	40	35	32	— 100 mm.
2^{50}	44	39.5	35.5	— " "
3^{05}	48.5	46	41	— "
3^{15}	57	54	50	—
3^{23}	} wt. of residue = 33.1 gms }			stop to change flasks (odor of HCl [illegible] & bother)
3^{27}				resume — 60-75 mls. left
3^{35}	64.5	59.5	52.5	— slow, hardly anything coming over 100 mm.
3^{53}	66	61.5	55	— rising



Time	Flask temp.	Lower Column	Upper column	Notes
3^{58}	65°	61°	60°	solid appe

① stop distillation to filter off Na_2SO_4 —
② filtrate deposits out crystals — decant (som
crystals suspended) —
③ Weight of remainder = 10.6 gms.
some of which may be hydroquin
about ½ grams of which were adde
to original distilland.

5^{35}	resume heating		—	30 m
5^{37}	40°	39°	35°	unstead
5^{40}	37°	33°	31°	falling
5^{41}	36	32.5	29	20 m
5^{43}	41	33	27.5	
5^{44}	50	34.5	~26	— STOP

nothing coming out

contains ice | fraction ③ = 8.1 gms. |
residue in flask = 2.2 gms.

6/6/5

Summary of Fractions

original distilland — 231.1 gms.

1st fraction	—	80.1 gms.
2nd "	—	118.3 "
3rd "	—	8.1 "
residue in flask	—	2.2 "
		208.7 "

unaccounted for — 22.4 gms. :— represented by precipitated salts, liquid lost in filtration and hold-up in column & condenser, etc.

Note : about 2 gms. hydroquinone added to initial distilland

① (boils at 286.2°)

② very small amount of ice in fraction ② ~~and~~ (about 1 gm.) and about 2 gms in fraction ③

6/6/5
83

2-24-47

Esterification of α-OH isobutyric acid

Purpose - repeat run of 2-4-47 using larger quantities

Procedure -

[I] Quantities,

1:4 mol ratio { 101.4 gms α-OH-isobutyric acid - 0.975 mol
125 " methanol - 3.91 "

50 - [Dried over CaSO₄]

29.7 gms anhydrous Na₂SO₄

[II] Procedure

3125 gms. MeOH of 125 gms. (A) total saturated with hydrogen chloride. The remainder of 93.75 gms. was used to dissolve the α-OH isobutyric acid & to slurry the Na₂SO₄; then the 31.25 gm portion of MeOH was added, and

the whole stirred for about 5 hours
following this heated for 2 hrs
at 50°

Start stirring at room temp. – 4^20 PM
Stop – 9^20 PM
then heated at 50° for 2 hrs.

(B) Distillation (2-25-47)

Atmospheric to strip Methanol
(thru Vigreaux column)

Fraction Flask te

① 63° to 70° 93.5 gms. – about
② 70° to 90° 59. 95° to
considerable refluxing at this point
column further distillate came over
indicating a high boiling residue.
Some Na_2SO_4 separated out as
6/16/

Na_2SO_4 filtered off —

2-26-47

Distillation under Vacuum

11^{10} — start heating at 100 mm.

	flask temp.	column temp.	notes
11^{25}	78	47	rising — 2/100 mm
		considerable reflux —	
11^{35}		at steady state	— 70 mm.
	77	35	100 mm.
11^{38}	80	45	
11^{45}	82	39	— 100 mm.
		Note: temp. dropped — distillate still coming over	
11^{50}	82	31	— 100 mm.
11^{55}	84	44	— 100 mms
12^{00}	86.5	41	— 100 mms
		reflux continuing	
12^{05}	87	35	100 mm.
12^{10}	89	33	no distillate — 100
12^{15}	95	60	50

Time	Flask Temp °C	Col. Temp °C	Vacuum
			30
12:00	82	53	25
12:05	89	45 crystals appearing,	28
12:12	90	started distillation	

2-28-47

α - OH isobutyric acid

Purpose :- ~~[illegible]~~ hydrolysis of cyanhydrin which had been stored in icebox

Procedure:-

$\boxed{I}$ Quantities :-

~~α-OH~~

cyanhydrin – 698 gms. (750 mls.)
(8.23 mols.)
con. HCl – 974 gms. (776 mls.)
(9.4 mols.)
(NH_3 to neutralize excess HCl = 82 mls.)

$\boxed{II}$ Operations

4^{35} - started adding HCl
5^{10} - solid appears
5^{20} - all HCl in

3-5-47

Purification of Crude Methylal

I Assume 25% of material is Me formate - Take 2000 mls. for this run.

Sp. g. = 0.871

MW of Me formate = 60

$$\frac{2000 \times 0.871 \times 0.25}{60} = 7.27 \text{ mols}$$

Me formate to be hydrolyzed

II 7.27 × 40 ≅ 291 gms. of NaOH needed

$$\frac{291}{30} = 970 \text{ mls. of } 30\% \text{ solution}$$

III Reflux for 4 hours, then take off fraction thru Vigreux - 41°-43°

3-18-47.

Purification of Crude Methylal

I $\frac{1700 \times 0.871 \times 0.25}{60} = 6.17$ mo

$6.17 \times 40 = 246.80$ gms. NaOH

$\frac{247}{30} = 8.2$ or 820 mls. of 30% solution

II Reflux for 4 hrs.

6/6/
27

3-11-47

α-OH isobutyric acid

Purpose - synthesis from cyanohydrin.

Procedure -

$\boxed{I}$ Quantities

cyanohydrin - 430 mls.
conc HCl - 445 "
conc. NH_3 to neutralize excess HCl - 43 mls.

$\boxed{II}$ Operations

Ⓐ 3-11-47 10^{30} } start adding HCl

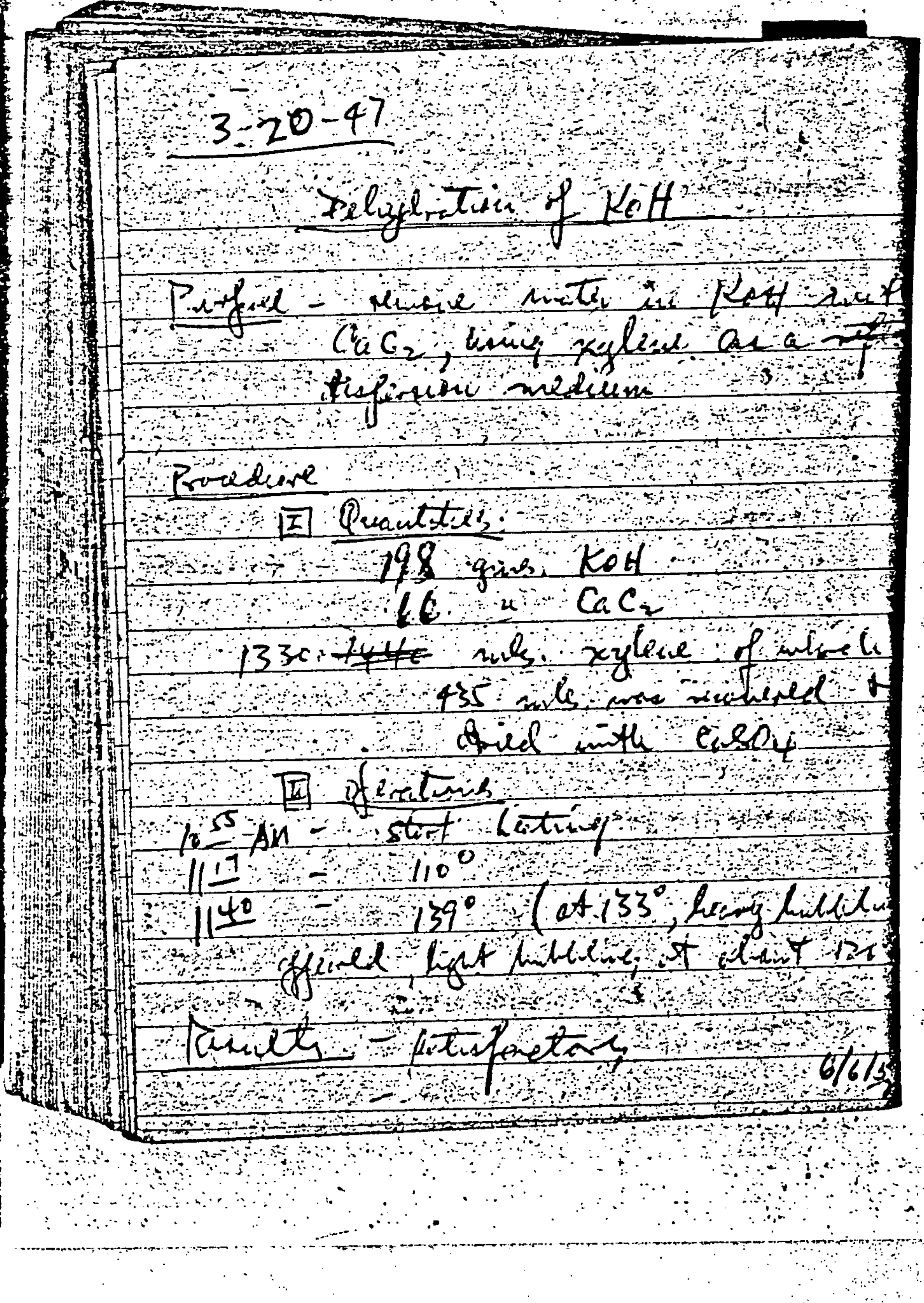
11^{05} - all in

2^{15} - off - permit to stay at room temp.

Ⓑ 3-12-47

11^{30} - start heating to 90°

11^{45} - 90° + - keep at 90° for 4 hrs.



3-20-47

Dehydration of KOH

Purpose - remove water in KOH wit
CaC$_2$, using xylene as a ~~[illegible]~~
dispersion medium

Procedure

I Quantities:

198 gms. KOH
66 " CaC$_2$
1330 ~~1440~~ mls. xylene of whic
435 mls was recovered +
dried with CaSO$_4$

II Operations

10^{55} AM - start heating
11^{17} - 110°
11^{40} - 139° (at 133°, heavy bubbl
effected, light bubbling at about 12

Results - satisfactory

6/6/5

3-25-47

Hexine Synthesis

Purpose – to prepare 2,5-hexyne-diol (yne 3, 4), from acetone + C_2H_2

Procedure

I Quantities –

118 gms. KOH
66 " CaC_2
450 cc. methylal
57 gms. of acetone

II Operations

A The dehydrated KOH-CaC_2 slurry in xylene was washed 3 times with ether to get rid of the xylene. The ether-KOH-CaC_2 slurry was then transferred to the reaction flask, most of the ether decanted

and the methylal added rapidly
over about 1/2 hr. keeping the
temp between 13°–15°, agitate 1 hr.

[B] The temp was then lowered to 0° + acetylene passed in for 20 minutes. The temp was then permitted to raise to 13°/ + the acetone passed in rapid and the same time acetylene addition resumed

[Note: During the period of temp rise acetylene continued to p out of the solution despite the stopping of the addition]

[C] 3^{oo} – start – when all acetone temp
3^{20} – 13°,
3^{40} – down to 10° + heat rise started rapidly, was to 14° then cooled to water bath

6/6

4^{05} - slurry becoming thick
& HEAT RISE - bath - -28° - (-16° / 17°)
internal temp - 15° & rising

4^{20} - 4^{25} - Note - Shutting down of the C_2H_2 stream at this point & heavy bubbling has 2 results:

bath temp. -33°

① the temp drops suddenly & quickly without continuance of the C_2H_2 addition after the temp drop causes it to RISE

② the mix becomes less fluid, i.e. with a rapid stream of C_2H_2 the agitator operated with ease & when the stream was cut off, the agitator started to move with difficulty & stop entirely

4^{25} - unstirrable element

4^{38} - internal temp = 7°

9-24-46

38
110

② 50 g Mon
1 g BP
2 g Gum arabic
400 g distilled water

205 to 1250 under mild reflux

As soon as peak period was reached heating was stopped and the powder was filtered. Washed three times in beaker and then washed three times by stirring for 1 hr each time.

Molding made of this material shows very little color (if any) but is hazy and full of bubbles.

) Same as above, but heated and stirred about 30 min after peak period.

Molding more hazy than in (2), but may contain less bubbles.

1/1/40

9.25.46

50g Mon.
2g Gum
1g BP
400 g ~~water~~ Saturated Salt soln (Salt in excess of Saturation)

Took 500 cc water and over 200 g of NaCl. Heated to 96°C and filtered. Temp. of filtrate about 90°C, therefore Salt is in excess of saturation at 82°C

9:30

Temp. 85°C at mild reflux
Washed 3 times in beaker and 3 times in flask with stirring

100 g Mon
2g BP
25 g Gum arabic
500 g water
12 N to 1:00
Dried at 78°C overnight. then raised to 100°C for

Much of the material was lost due to agglomeration which was stuck to flask. Too much Mon. for the amount of water

)

9-24-46

50 g Mon

1 g BP

2 g Gum arabic

400 g distilled water

$\frac{95}{110}$

205 to 1250 under mild reflux

s soon as peak period was reached
ating was stopped and the powder
as filtered. Washed three times in
eaker and then washed three times
y stirring for 1 hr each time.

molding made of this material shows
ery little color (yellow) but is hazy and full
bubbles.

Same as above, but heated and stirred about 30 min
fter peak period

Molding more hazy than in (2), but may
ontain less bubbles.

9-26-46

① 50 g Man
2 g Agar
1 g BP
400 g Water

1250 to 1:40
Reflux stopped at 1:20 while bath was 88°C

Filtrate very milky.
Much of the material stuck to the sides of flask but was easily powdered

Very little of the material are round pearls, most of it appears like being shreded.

7 7 wastes

1. Sat. salt, excess salt

Cut down on H_2O

2. {100 Mon
2 BP
2% gum arabic
400 g water}

3. ~~1% agar on water~~

40 Mon
1 BP
2 Gum arabic
400 H_2O
} disconnect at max

400 H_2O boil

4. Agar 1%

40 Mon
1 BP
400 H_2O
2 g Agar

100 g Mo[illegible]
2 g BP
3 g Gum arabic
800 g Water

Started 3.45

1247.1
Tare 1248.2
95.5

6/6/50

9-13-46

50 g mon
1.0 BP
1.5 gum arabic
400g water
Pan at 77-80°C

Result: very Fine powder
Turned yellow on drying (mat'l fused)

9-13-46

100 g mon
2g BP
0.8 g Gum arabic
400 g water (distilled)

Started 11:15	Bath	Mix	
50	78	68	reflux starts
30	85	79	

Agglomeration

---

100 g mon
2g BP
1.5g Gum arabic
500 g water
135 started 735 stirring

#9

50 ~~100~~ gms. Monomer MaMs

1.5 ~~3~~ gms. B.P.

1.5 ~~3~~ gms. Gum Arabic

400 ~~300~~ gms. H_2O

Start $10^{\frac{10}{PM}}$ Temp. 75° → 80°

[illegible] 11:30

Finish 10 [illegible]

9-17-46

#6

100 gms. Monomer MeMe

1 gm. B.P

3 gms. Gum arabic — mold

800 gms. H_2O

Start 12^{00} NOON   Temp. 76° → 80°

Finish 1^{15} PM

#7

100 gms. monomer MeMe — mold

0.5 gms. B.P.

3 gms. Gum arabic

800 gms. H_2O

Start 3^{50} Temp. 74° → 80°

Finish 5^{50}

8

100 gms. Monomer MeMe

3.0 gms. B.P.

30 gms. Gum arabic

800 gms. H_2O

Start 8^{05} Act. 8:35   Temp. 73° → 80°

Finish 8^{50}

9-16-46

100 g Main

2g BP

4.5 g Gum Arabic

900 g water

3.50 to 4.50 at 80°

6-16-46

100g Mon (washed)
2g BP
4g Gum arabic
800g Water

11.15 started — finished 12.30

Temperature 80-82°C
Coarser powder than RH; fairly uniform in size

100g MeMe Mon (washed)
2g BP
5g Gum arabic
1000g water

Started at 1.45 — Finished at 2.50
Temp. 80-82°C
Much of the polymerized matl is stable emulsion

[illegible]

10
11 } Screenings
12

3.1
38.4
4
153.6

bot (TOP)
15 + 16

9-9-46

Dissolved 153 g of NaCl in 400 g of distilled water, filtered, and added 2 g of gum arabic then added 50 g mon with 1 g BP.

12.35 to 1.30 at 80°C

Finer powder than in cases where no NaCl was used. Washed with dist. water

17

Same as above

2.30 to 3.30 at 80°C

Washed with NaCl soln + then with water (5 times)

[illegible] g

84.79
moisture test 82.59
2.20

13 2 - 6 washes (may be 8)

5-19-46

13.414

Cleaning again

7-20-

2
2
2
4
4
4

26
4

30
2
2
2

36
4

40

50 g. Monomer
1 g. B.P.
40 g. Gum arabic
400 g. H₂O

Note - very frothy
→ foaming point of boiling

Start 1:35 PM Temp 71-72°C
Finish

"
"

65-4327
Ex 16

SAC, Philadelphia 7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (5) (Exhibit 16)

On 6/25/50, GOLD examined the above exhibit and stated that this photostat was in connection with one of BROTHMAN's processes and that this photostat had been secured from the New York City Public Library.

EXHIBIT 65-4307-1B-13 (5) (Exhibit 17)

On the same date GOLD examined the above photostat and stated that this was another patent which had been photostated at the New York City Public Library and that this patent referred to styrene, but its use in connection with plastics rather than the Buna S. process. This patent had been photostated in connection with work being done by the BROTHMAN laboratory.

TSM:HKF
65-4307

Patented Feb. 18, 1936 **2,030,901**

UNITED STATES PATENT OFFICE

2,030,901

PROCESS FOR DEPOLYMERIZING ALPHA SUBSTITUTED ACRYLIC ACID ESTERS

Daniel E. Strain, Wilmington, Del., assignor to
Du Pont Viscoloid Company, Wilmington, Del.,
a corporation of Delaware

No Drawing. Application January 10, 1935,
Serial No. 1,153

13 Claims. (Cl. 260—106)

This invention relates to a depolymerization process and, more particularly, to a method of producing a monomeric ester of alpha substituted acrylic acid from the corresponding polymeric ester.

The use of polymeric esters of alpha substituted acrylic acids for various purposes in the coating and plastic arts is known. In the use of such material there is inevitably a certain amount of scrap polymerized resin which will be wasted if it cannot be reduced to the monomeric form. This is particularly true of the resins which are used in the various turnery processes. To be able to recover monomeric ester from such scrap material is of great importance in the economical processing of these polymeric esters.

Heretofore it has been known in the art that polymeric methyl acrylate cannot be depolymerized by dry distillation, the first fraction from such distillation allegedly consisting of dimer, the second fraction trimer, and so on. Investigations have also shown that such polymeric substances as polymeric alkyl acrylates generally and even polymethacrylic acid cannot be depolymerized by dry distillation to give the corresponding monomeric compound.

An object of the present invention is to provide a simple and economical method of producing the monomeric esters of alpha substituted acrylic acid from the corresponding polymers. A further object is to provide a method for recovering monomeric ester of alpha substituted acrylic acid from scrap pieces of the corresponding polymer such as may accumulate in the production of articles from the polymer, particularly in the production of articles by turnery processes.

The above objects are accomplished according to the present invention by heating a polymeric ester of alpha substituted acrylic acid at a temperature above its decomposition point and condensing the vapors resulting therefrom. In a practical specific embodiment, the polymeric ester is heated at substantially atmospheric pressure to a temperature substantially above its decomposition point, the vapors resulting from such distillation are condensed, and the condensate is fractionally distilled to recover the monomeric ester in substantially pure form.

The following examples are given to illustrate specific embodiments of the invention. In these examples the polymeric ester is subjected to what is commonly known as "dry distillation."

Example 1.—70 grams of methyl methacrylate polymer were placed in a one liter distilling flask fitted with a thermometer and a water condenser, and subjected to dry distillation over a free flame. 68 grams of liquid condensate were collected and fractionated, from which 62 grams of methyl methacrylate monomer were obtained. The monomeric methyl methacrylate so collected, polymerized to a solid resin when heated for 15 minutes at 100° C. in the presence of 1% benzoyl peroxide.

Example 2.—16 grams of n-butyl methacrylate polymer were heated as in Example 1 and 15.5 grams of distillate collected, from which 12 grams of n-butyl methacrylate monomer were obtained. This material polymerized to a solid resin when heated for 35 minutes at 100° C. in the presence of 1% benzoyl peroxide.

Example 3.—9½ grams of ethylene glycol dimethacrylate were heated as in Example 1, and 7.5 grams of liquid condensate were collected. Upon fractional distillation 6 grams of monomeric ethylene glycol dimethacrylate were obtained. This material readily polymerized when heated at 100° C. in the presence of 1% benzoyl peroxide.

Example 4.—Polymeric butoxyethoxyethyl methacrylate is dry distilled as in Example 1 and the monomer obtained by fractionally distilling. This monomer has a boiling point of 116° C. at 4 mm. pressure and is readily polymerized by heating at 65° C. for 48 hours in the presence of benzoyl peroxide.

Example 5.—Polymeric stearyl methacrylate is dry distilled as in Example 1 and the condensate fractionally distilled to recover the monomer. This monomer has a melting point of 28-29° C. and is readily polymerized by heating at 65° C. for 2 days in the presence of benzoyl peroxide.

In any of the above examples the process of polymerization and depolymerization may be repeated any number of times without adversely affecting the polymerizing qualities of the monomer.

It is to be understood that the above examples are merely illustrative and that by heating any polymeric ester of alpha substituted acrylic acid at a temperature above its decomposition point the corresponding monomeric ester may be obtained. Among the esters of this class may be mentioned the following: beta-chloroethyl methacrylate, o-cresyl methacrylate, p-cyclohexyl phenyl methacrylate, decahydro beta-naphthyl methacrylate, decamethylene glycol dimethacrylate, beta-diethyl amino-ethyl methacrylate, diethylene glycol dimethacrylate, diisopropyl carbinol methacrylate, glycol monomethacrylate, furfuryl methacrylate, isobutyl methacrylate, lauryl methacrylate, methyl allyl methacrylate, naphthenyl methacrylate, oleyl methacrylate, beta-phenylethyl methacrylate, resorcinol dimethacrylate, secondary-butyl methacrylate, tetrahydrofurfuryl methacrylate, tertiary-butyl methacrylate, glycol di(alpha-butylacrylate), benzyl ethacrylate, ethyl-alpha-phenylacrylate, methyl-α-isopropylacrylate, methyl-α-heptylacrylate, methyl-α-methylphenylacrylate, ethyl-αmethylcyclohexylacrylate, and propyl-α-cyclohexylacrylate. The above mentioned esters fully illustrate the applicability of the present invention to the class of polymerized esters of alpha substituted acrylic acid, including the alpha alkyl substituted, alpha aryl substituted, and alpha aralkyl substituted acrylic acids.

While, in the examples given above, only simple dry distillation of the polymeric ester at substantially atmospheric pressure is illustrated, the present method may be carried out at elevated pressures to effect heat-cracking prior to distillation. Also, the dry distillation may be carried out at reduced pressures, if desired. Instead of distilling as shown in the examples, so-called "flash distillation" may be employed where the polymeric ester is slowly introduced on to a highly heated surface and instantly vaporized. Variations in specific details of the dry distillation, condensation, and fractional distillation to recover the monomer in substantially pure form will occur to those skilled in the art. As will be understood, the polymeric material must be heated to a temperature above its decomposition point at the pressure employed and, generally, for economical operation, the material should be heated appreciably above such decomposition point. Specific temperatures employed must, necessarily, be governed by the particular polymer being depolymerized. Ordinarily the vapors of the monomeric compound will be condensed but, if desired, the vapors may be used directly with some other reactant.

The present process is useful for the recovery of monomeric ester from the corresponding polymer regardless of its source. The process is particularly useful for the recovery of scrap resin in the turnery processes where waste from scrap constitutes a major production cost item. However, the process also finds utility in the recovery of monomer either from poor quality polymer or accidentally set up material, as well as from polymer of any other source.

The fact that the monomer can be recovered by dry distillation of the polymeric esters herein disclosed is most unexpected in view of the behavior of such closely related compounds as polymeric alkyl acrylates and polymethacrylic acid. Despite the fact that the polymeric alkyl acrylates and polymethacrylic acid cannot be dry distilled to recover the corresponding monomer, yet the present process is applicable to the whole class of polymeric esters of alpha substituted acrylic acid as far as can be ascertained from the behavior of the esters herein disclosed.

As many apparently widely different embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention is not limited to the specific embodiments thereof except as defined in the appended claims.

I claim:

1. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester at a temperature above its decomposition point.

2. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

3. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester at a temperature above its decomposition point, condensing the vapors resulting therefrom, and fractionally distilling the condensate to recover the monomeric ester in substantially pure form.

4. Method of producing a monomeric ester of alpha alkyl substituted acrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

5. Method of producing a monomeric alkyl ester of alpha alkyl substituted acrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

6. Method of producing a monomeric ester of methacrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

7. Method of producing monomeric methyl methacrylate comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

8. Method of producing monomeric methyl methacrylate comprising heating the corresponding polymeric ester at a temperature above its decomposition point, condensing the vapors resulting therefrom, and fractionally distilling the condensate to recover the monomeric ester in substantially pure form.

9. Method of producing a monomeric ester of alpha aryl substituted acrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

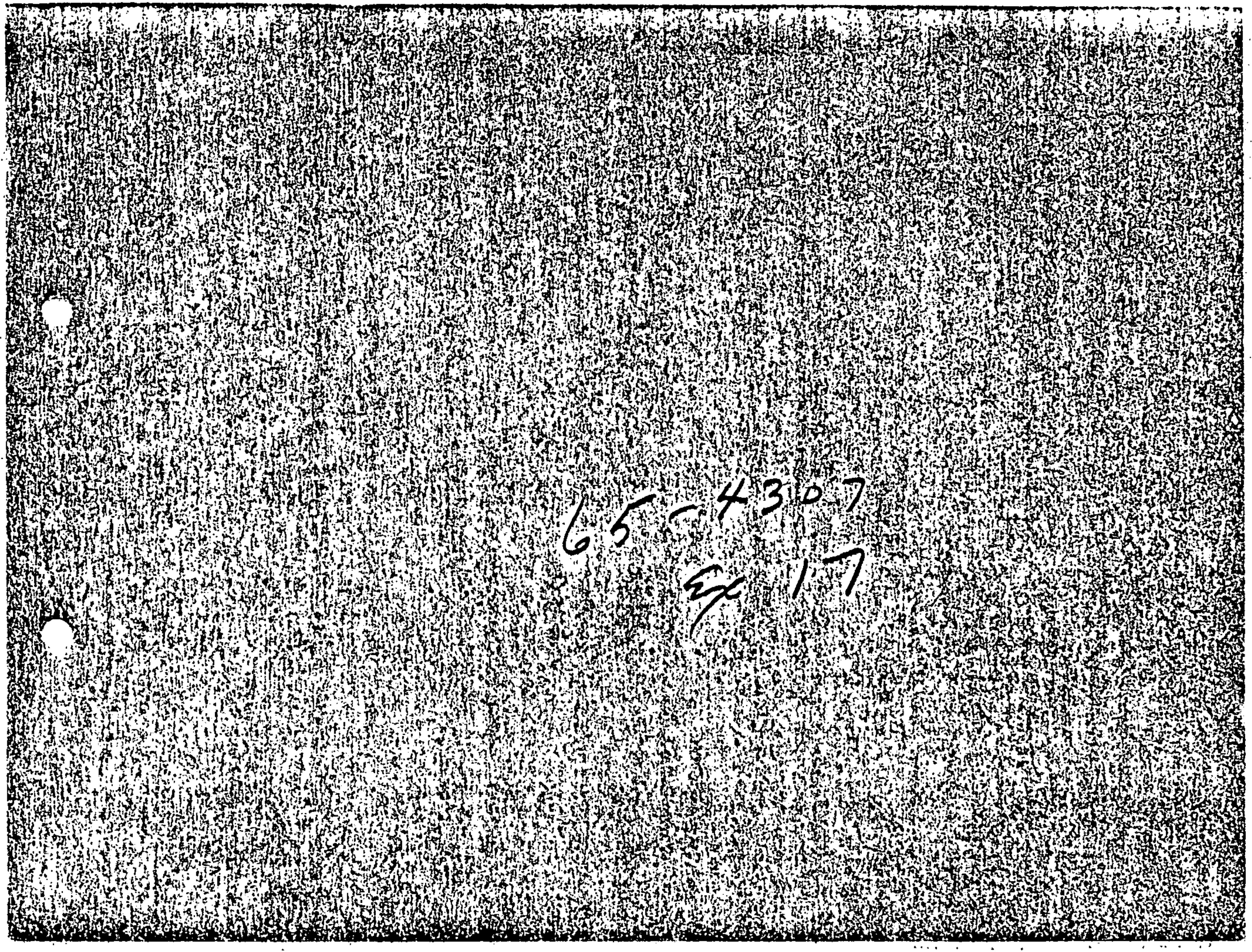
10. Method of producing a monomeric ester of alpha aralkyl substituted acrylic acid comprising heating the corresponding polymeric ester at a temperature above its decomposition point and condensing the vapors resulting therefrom.

11. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester at substantially atmospheric pressure and at a temperature above its decomposition point, condensing the vapors resulting therefrom, and fractionally distilling the condensate to recover the monomeric ester in substantially pure form.

12. Method of producing monomeric methyl methacrylate comprising heating the corresponding polymeric ester at substantially atmospheric pressure and at a temperature above its decomposition point, condensing the vapors resulting therefrom, and fractionally distilling the condensate to recover the monomeric methyl methacrylate in substantially pure form.

13. Method of producing a monomeric ester of an acrylic acid substituted in the alpha position by a hydrocarbon radical which comprises heating the corresponding polymeric ester under reduced pressure and at a temperature above its decomposition point, and condensing the vapors resulting therefrom.

DANIEL E. STRAIN.



65-4307
Ex 17

SAC, Philadelphia 7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (5) (Exhibit 16)

On 6/25/50, GOLD examined the above exhibit and stated that this photostat was in connection with one of BROTHMAN's processes and that this photostat had been secured from the New York City Public Library.

EXHIBIT 65-4307-1B-13 (5) (Exhibit 17)

On the same date GOLD examined the above photostat and stated that this was another patent which had been photostated at the New York City Public Library and that this patent referred to styrene, but its use in connection with plastics rather than the Buna S. process. This patent had been photostated in connection with work being done by the BROTHMAN laboratory.

TSM:HKF
65-4307

Patented Sept. 26, 1944 **2,359,212**

UNITED STATES PATENT OFFICE

2,359,212

PROCESS FOR DEPOLYMERIZING POLYSTYRENE

Joseph C. Frank and James L. Amos, Midland, and
Albert F. Straubel, Auburn, Mich., assignors to
The Dow Chemical Company, Midland, Mich.,
a corporation of Michigan

No Drawing. Application September 17, 1941,
Serial No. 411,150

3 Claims. (Cl. 260—669)

This invention relates to a method for the depolymerization of polystyrene to produce lower styrene polymers and monomeric styrene.

In the commercial preparation and use of solid resinous polystyrene, e. g., for the manufacture of molded articles, a problem of economic importance is the utilization of trimmings, off-grade batches, and other types of scrap material. One method that has been suggested for the profitable utilization of such material is its depolymerization to the lower polymeric forms by heating. Such depolymerization of polystyrene has also been shown to be of importance as one step in a method for the recovery of styrene from drip oil, cracked petroleum fractions, and the like, where the styrene is present in low concentrations and usually associated with other compounds boiling over the same range as styrene. Thus, a styrene-containing fraction obtained from such sources may be treated to polymerize the styrene to a high molecular weight product which may then be separated from the fraction and depolymerized by direct heating to styrene and lower polymers which may then be purified or utilized in known manner.

The pyrolysis of polystyrene has not heretofore been commercially feasible due principally to the extremely low heat conductivity of polystyrene and the consequent difficulty of heating the main body of the material without overheating the outer layers. It has been shown that when the depolymerization is carried out by heating the polystyrene under vacuum to remove the styrene and lower polymers rapidly from the hot zone, a longer heating period is required and little, if any, decrease in the amount of by-products formed is obtained. When the pyrolysis is carried out by such previously known methods there are formed, in addition to styrene and its lower polymeric forms, appreciable quantities of undesirable hydrocarbons, e. g., 1,3-diphenylpropane, 1,3,5-triphenylpentane, 1,3,5-triphenylbenzene and toluene, together with ten to twenty per cent of tarry residue.

We have now found that polystyrene may be depolymerized rapidly, and with the production of only minor amounts of by-products, by subjecting it to the action of superheated steam. The depolymerization is usually carried out by placing the polystyrene in a vessel fitted with a condenser and receiver and intimately contacting the superheated steam with it. Solid polystyrene may be broken up and fed continuously into the depolymerization vessel and be subjected to the action of steam in the solid or semi-solid state. Liquid polymeric styrene may be run into the depolymerization vessel and superheated steam blown through the liquid, or it may be treated with steam counter-currently in a tower. The monomeric styrene vapors together, usually with considerable amounts of the lower polymeric forms of styrene and the steam may be condensed and collected in the receiver or they may be fractionally condensed to separate the lower polymers from the styrene.

The depolymerization is usually carried out at atmospheric pressure, although higher or lower pressures may be used if desired. Steam at a temperature between 250° and 600° C., preferably between 300° and 450° C. is used in the process. Although the amount of steam used relative to the amount of polystyrene depends upon several factors, e. g., the rate of flow of the steam, the degree of contact between the polystyrene and the steam and the particular temperature used, it is usually from five to twenty-five times the weight of the polystyrene, and may be more or less than this amount.

The oily layer in the receiver may be separated from the aqueous layer and treated in any suitable manner, e. g., by steam distilling, to separate the monomeric styrene. Lower polymeric forms of styrene may be fed back into the process to produce additional monomeric styrene, if desired, or the oil remaining after steam distilling the monomeric styrene may be fractionally distilled to isolate fractions rich in a single lower polymer of styrene, e. g., the dimer, the trimer, or the tetramer, which may be collected as final products.

The following examples will serve to illustrate the principles of the invention, but are not to be construed as limiting its scope.

Example 1

4590 grams of polystyrene was placed in an iron reactor fitted with a condenser and receiver. 60,780 grams of steam at a temperature of 350° C. and at atmospheric pressure was passed through the reactor. 4321 grams of oily material were separated from the water in the receiver. This was a recovery of 93.4 per cent based on the polystyrene used. The oily layer from the receiver was fractionally distilled to recover monomeric styrene. There was thus obtained 2250 grams of the latter compound of 23.4 per cent purity or a 61.4 per cent yield on the basis of the polystyrene started with. The residue from the fractional distillation was fed back into a subsequent depolymerization experiment.

Example 2

5495 grams of polystyrene was treated with 60,370 grams of steam at 340–360° C. and at atmospheric pressure as in Example 1. The oily layer which collected in the receiver weighed 5185 grams which was a recovery of 94.5 per cent on the basis of the polystyrene used. The oily layer was fractionally distilled and found to contain 52.6 per cent of monomeric styrene, 22.2 per cent of dimeric styrene, 18.8 per cent of trimeric styrene, and 2.4 per cent of tetrameric styrene.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the method herein disclosed, provided the step or steps stated by any of the following claims or the equivalent of such stated step or steps be employed.

We therefore particularly point out and distinctly claim as our invention:

1. The method which comprises heating polystyrene to a depolymerizing temperature between 350° and 600° C. by passing superheated steam of at least as high a temperature into contact therewith and condensing the styrene which is evolved together with the steam.

2. In a method of depolymerizing polystyrene, the steps of heating the latter to a depolymerizing temperature between 300° and 450° C. by passing steam which has been superheated to a temperature higher than the depolymerizing temperature into intimate contact with the polystyrene, condensing the evolved depolymerization products and fractionally distilling the latter to recover therefrom a fraction of styrene and another fraction of dimeric styrene.

JOSEPH C. FRANK.
JAMES L. AMOS.
ALBERT F. STRAUBEL.

65-4307-1B-13 ([illegible])

65-74307

Ex 18

7/10/50

SAC, Philadelphia

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (7) (Exhibit 18)

On 6/25/50, GOLD identified this booklet as having been obtained from the BROTHMAN laboratory sometime while he was employed there. He said this booklet is merely one of government specifications on plastics.

TSM:HKP
65-4307

65-4307
Ex 19

SAC, Philadelphia 7/10/50

SA T. SCOTT MILLER, JR.

HARRY GOLD, was.
ESPIONAGE - R

EXHIBIT 65-4307-1B-13 (8) (Exhibit 19)

On 6/22/50, GOLD examined the above material and stated that it was concerned with the patent applied for by BROTHMAN in connection with the thioglycolic acid process used in the STANTON LABORATORY.

GOLD stated that the copy was given to him for him to check.

TSM:HKF
65-4307

THE COOPER ALLOY FOUNDRY CO.
BLOY ST. & RAMSEY AVE.
HILLSIDE, N. J.

A. BROTHMAN & ASSOCIATES
29-28 - 41ST AVE.
LONG ISLAND CITY, N.Y.
ATT - PURCHASING AGT.

IMPORTANT
RICE REVISION

MEMORANDUM FOR THE PREPARATION OF THIOGLYCOLIC ACID PATENT PAPERS

THE INVENTION

Our invention consists of a continuous process for the manufacture of thioglycolic acid by the following steps:

1. Saturating a solution of NaOH with H_2S under "super-atmospheric" pressures to form a solution of sodium hydrosulfide containing a sharp excess of H_2S in solution. (See Equation #1 below.)

2. Reacting the sodium hydrosulfide solution containing the excess of H_2S as obtained from #1 above with an aqueous solution of sodium chloracetate, maintaining the reaction system under a pressure of H_2S equal to that at which the NaOH solution was originally saturated. (See Equation #2 below.)

3. Subjecting the reaction product liquor obtained from #2 above to a "flash" relief from the excess H_2S by leading the liquor from #2 above to a flash column operated under atmospheric pressure and by simultaneously establishing contact in the column between the product liquor from #2 and an excess of H_2SO_4. (See Equation #3 below.)

$$NaOH + H_2S \longrightarrow NaHS + HOH \qquad (1)$$

$$NaHS + ClCH_2COONa \longrightarrow NaCl + HSCH_2COONa \qquad (2)$$

$$HSCH_2COONa + H_2SO_4 \longrightarrow Na_2SO_4 + HSCH_2COOH \qquad (3)$$

THE ADVANTAGES OBTAINED BY OUR INVENTION

The advantages offered by our invention over all previously described methods of producing thioglycolic acid are:-

1. A lower raw materials cost per pound of finished product which reflects a higher yield from chloracetic acid, soda ash, caustic soda and H_2S.

2. Absolute and assured uniformity of performance of the process.

3. Freedom from appreciable amounts of chloracetic acid, glycolic acid,

and thiodiglycolic acid as impurities in the final product, thereby permitting isolation of the end product in commercially useable form by an extraction operation alone, rather than by an extraction operation followed by a distillation operation. (Note:- The isolation of thioglycolic acid from the above-mentioned impurities by distillation is an exceedingly difficult and costly operation.)

4. Complete freedom from dithioglycolic acid in the end product, thereby eliminating the cost of reducing this impurity to thioglycolic acid.

5. Complete freedom from obnoxious odors through the operation of a closed system involving recycling of the excess H_2S.

6. For any given plant capacity, a lower cost for plant equipment in view of the extraordinary yields obtained by us and in view of the smaller size equipment involved in operating the process on a continuous production basis.

DESCRIPTION OF THE INVENTION

The following is a description of the process as laid out on Flow Sheet #SL-B-101 for a plant with a production capacity of 30,000 lbs. per month of thioglycolic acid, based on a 25-day month and an 8-hour day.

The Preparation of Sodium Chloracetate

The preparation of the requisite sodium chloracetate is a batchwise, semi-automatic operation involving:

1. The automatic charging of the vessel, E1, with a required amount of water-of-solution.

2. The manual charging, guided by the instrumentation attached to E1, of the required amount of chloracetic acid and the dissolution of the same in the water-of-solution.

3. The automatic addition of soda ash crystals to E1 to convert the chloracetic acid to sodium chloracetate.

Upon receipt of an electrical impulse from Level Instrument, C2,[1] which impulse is obtained by the baring of the lower probe member of this instrument, water is admitted through Valve V1 to the height of the upper probe member of C2. Simultaneously with the opening of Valve V1 and for the duration of the water-filling operation, the annunciator, C45, is sounded, calling the operator's attention to the necessity of charging the unit E1 with the appropriate amount of chloracetic acid.

The Level Instrument, C3, the lower probe of which is located at the same level as the lower probe of C2 will, upon baring of its lower probe, set up a flow of current from power supply to A' through B' to ground, which condition of flow will persist until the charging of the proper amount of chloracetic acid to K1 results in the submerging of C3's upper probe member, at which time the flow of current to A' through B' is interrupted and a flow from power supply to C' through D' to ground is established as the condition in force until an exhausting of K1's contents bares C3's lower probe again.

It will thus be seen that the lowering of the liquid level in K1 to the level of the lower probes of C2 and C3 initiates the charging of K1 with an appropriate amount of water, (as defined by the vertical distance between upper and lower probes of C2) and the starting of the agitator drive of K1 (via the flow of current in C3 to A' through B' to ground) through the activation of the pilot switch in the starter member of the power supply circuit for the agitator drive via the parallel power supply for the pilot switch through "A".

1/ Level Instrument C2 is a standard, commercial, electronic instrument of the "pump-up" type manufactured by the Photoswitch Co. Referring to the wiring diagram for K1 and with particular reference to the wiring diagram for the instrument, C2, it will be noticed that C2 is essentially a two-wire type control. The sensitised elements of the instrument consist of two probes, each of which is located at appropriate levels in a tank chamber. The essential nature of the electrical circuit involved is such that alternative closing of two distinct and alternative two-wire circuits is alternatively signalled by each of the two probes. The closing of the circuit between either probe and its conjunctive ground involves, through a lock-in type relay, the closing of one circuit and the opening of the other. In C2, from the time of submergence of the upper probe to the time of baring of the lower probe, current flows from power supply to A through B to ground. When the lower probe is bared again, current flows from power supply to C through D to ground, (while the previously-mentioned circuit is signalled into an open position), until the upper probe becomes submerged.

In series with the aforementioned pilot switch is the signal light, C1, which by remaining lit through the period from the initiation of water-filling to the completion of the chloracetic acid addition (until the upper probe of C3 is submerged), guides the manual addition of this material by the attendant laborer from barrels brought up by him from raw material storage by the traveling hoist. The filling of E1 with an appropriate quantity of chloracetic acid will cause the submersion of the upper probe member of C3 and the establishing of a flow of current from power supply to C' through D' to ground, while simultaneously interrupting the flow of the alternative circuit to A' through B' to ground.2/

From the wiring diagram from C3 and from the fact that the circuit from power supply to C' through D' to ground remains in force for the entire period from the submersion of the upper probe member of C3 to the baring of the lower probe member of C3, it will be seen that the relay, C6, is thrown into action for the whole period starting from the completion of the addition of the requisite amount of chloracetic acid to the exhausting of the contents of E1. The actions of the relay, C6, are:

1. Through the power contacts "F", it conditions the master switch circuit (see the wiring diagram for relay C8), thus imposing upon that circuit the condition that it cannot be brought into force without addition of the chlracetic acid to E1.

2. Through the power contacts, "G", it conditions the circuit for the application of heat to the contents of E1, (see wiring diagram for V7), thereby eliminating the possibility of the waste of steam thru the heating of either a charge of water or an empty tank in E1.

3. Through the power contacts, "H", it qualifies the circuit for the starting of Pump P1, eliminating the possibility of starting up the Pump P1 without completing the chloracetic acid addition cycle. It will be seen from the wiring diagram for the pilot switch, C7, and the valve, V2, that the timer, C5, and the relay E8 in the master switch circuit, become thereby the only possible interrupting factors for the starting up of the Pump P1 and the opening of the Valve, V2. That is to say, all other conditions upon the master switch

---

2/ It will thus be seen that C3 functions essentially in reverse sequence to that described for C2, and is therefore called a "pump-down" unit.

circuit having been fulfilled, the motivation of F1 and V2 must still wait upon the completion of the soda ash addition operation as guided by C5.

h. Through the power contacts, "I", it initiates the operation of the Timer, C5.

Since the Timer C5, in its turn, does the following:

a. Through the power contacts, "J", it closes the circuit for the vibrator component, C4, of the constant-rate-solids-feed-device attached to the soda ash hopper E2, it provides for the addition of the soda ash in prescribed quantity over a prescribed period.

b. Through power contacts, "K", it interrupts the circuit for the pilot switch, C7, and the valve, V2, thereby preventing the starting-up of feeding of the contents of E1 to the system prior to completion of the soda ash addition cycle.

c. Through the power contacts, "B", it closes the parallel power supply circuit of the pilot switch for the agitator, E1, thereby providing for the passing of the activation of the agitator drive of E1 from the dead circuit fom A' through B' to ground, to the live circuit from C' through D' to ground, (thus providing for the maintenance of agitation thru the period of the soda ash addition cycle).

d. Through the operation of the power contacts, "E", it provides for the conditioning of the master switch circuit (see wiring diagram for relay C8) to the end that the plant cannot be set into operation until the soda ash addition cycle has been completed.

The stoichiometric equivalent of soda ash to the amount of chloracetic acid added to E1 is added over a period of one hour at a constant rate through the constant-rate-solids-feed-device attached to the soda ash hopper, E2. Both the period of addition of the soda ash and the use of the constant rate addition principle guard against a "frothing over" through the generation of CO_2.

A study of the above-described circuits will indicate that:

1. The replenishing of the supply of sodium chloracetate is automatically signalled, upon the exhaustion of the previous batch of sodium chloracetate solution. This occurs in stages involving the following sequence:

   a. Automatic addition of the requisite amount of water;

   b. The signalling of the operator to add the required amount of chloracetic acid while providing for the guiding of the operator in adding the requisite amount of chloracetic acid;

   c. The automatic raising of the temperatures of the mass in E1 to the desired 50 C. during the progress of the soda ash addition operation, thereby providing for the readiness of the batch of sodium chloracetate for addition to the system upon completion of the soda ash addition cycle, by providing for the completion of the reaction to form the sodium chloracetate.

d. The automatic addition of the requisite amount of soda ash subject to the qualification that the chloracetic acid has been previously added in the required amount.

2. Provides safeguards against:

   a. The wastage of steam in heating either an empty tank or a batch of water in E1.

   b. The starting up of the plant without the operator's having made the addition of the chloracetic acid in the required amount to E1.

   c. The starting up of the plant without having carried out the conversion of the chloracetic acid to sodium chloracetate.

3. Confines the period of operation of the agitator to the period during which chloracetic acid is being dissolved in water and the period during which the chloracetic acid is converted to sodium chloracetate.

There remains now but to mention that the maintaining of the influent stream of sodium chloracetate at the required temperature for the optimum effecting of the sodium chloracetate-sodium hydrosulfide reaction, namely 50° C., is accomplished through the "on-off" control of Valve V7 through the temperature control C31, which is the sole controlling factor over the operation of Valve V7 through power contacts "C" of the relay, C6, after the initiation of soda ash addition cycle up until the exhaustion of the prepared batch of sodium chloracetate has been exhausted. The operation of a plant producing 30,000 lbs. of thioglycolic acid per 8-hour day, 25-day month, and based upon the preparation of a single batch of sodium chloracetate to provide for the entire shift, involves:

1. The preparation of 624 gals. of sodium chloracetate solution made up through the addition of 1,940 lbs. of chloracetic acid to 490 gals. of water, and the treatment of the resultant solution with 1,085 lbs. of soda ash with a final temperature for the resultant solution of 50° C. being obtained in order to assure completion of the conversion to sodium chloracetate.

2. The application of a 2-HP dual marine-propeller type mixer assembly to the contents of E1 during the dissolution of the chloracetic acid in water and the conversion of chloracetic acid to sodium chloracetate.

3. The use of approximately 49 sq.ft. of heat exchange surface in the form of an internal helically-wound coil for the raising of the temperature of the final solution to 50° C., during one hour, when 240° F. steam is employed as the heating medium.

The Continuous Preparation of Sodium Hydrosulfide

The system for the preparation of H_2S-surcharged sodium hydrosulfide solution actually comprises:-

1. A unit for the continuous feeding of sodium hydroxide in proper concentration in aqueous solution to an absorption column.
2. An "absorption" unit for the contacting of the sodium hydroxide solution from (1) above with H_2S for the purpose of forming the sodium hydrosulfide and surcharging a solution of the same with H_2S.
3. A unit for continuously generating the required H_2S to the demand rate of the system.
4. A system for "conditioning" (de-watering) the recycle surcharged H_2S as reclaimed from the H_2S Flash System.

The sodium hydrosulfide is formed in such quantities as to be present in 10% excess over stoichiometric requirements for the reaction with the sodium chloracetate. The pressure of H_2S over the system is 220 psig, at which pressure a surcharging of the system to the extent of approximately 0.28 lbs. of H_2S (as H_2S in a state of dissolution in the sodium hydrosulfide solution) per pound of thioglycolic acid produced finally is involved.

The preparation of sodium hydrosulfide solution, which is synonymous with the starting up of the plant, involves the throwing of the master switch, C16, (see wiring diagram for relay C2). Observing the wiring diagram, it will be apparent that the throwing of the master switch, C16, accomplishes the following:

1. Through a circuit from power supply to A" through B" to ground,
    a. The pilot switch for the agitator on E12 is thrown into operation. This assures the best conditions for the rapid assumption by the material in E12 (the sump component of the H_2S Flash System) of

"steady-state" temperature during the plant start-up heating of this material.

b. The air pilot, C21, athwart the pneumatic circuit from the temperature instrument, C37, to the controlled steam input valve, V13, is opened, thus applying heat to the material in E12, to provide for the achievement of "steady-state" temperature mentioned in (a) above.

c. The air pilot, C20, athwart the pneumatic control line from the flow instrument, C36, to the controlled valve, V11, is opened, providing for the assumption of "steady-state" conditions by the gas phase in the flash column, E11.

d. The air pilot, C28, controlling the pneumatic transmission from the temperature instrument, C41, on the condenser, E16 to the control valve, V23, is opened, providing for the condensing of water from the gaseous effluent sent from E11 to E16.

2. Upon assumption of steady-state temperature conditions in E12, as assured by the opening of the air pilot C21 and as detected by the temperature instrument C37 (the pneumatic signal from which is converted to an electrical signal through the pressure switch C22), with the assurance that water in appropriate amounts will be provided to the condenser E16 (through the opening of the air pilot C28), with the assurance that steam will be furnished in the appropriate rate of supply as controlled by the flow instrument C36 to the internal coil of the Flash Column (because of the opening of the pilot valve C20), with the assurance (through the contacts "F" of the relay C6 and the contacts "E" of the timer circuit C5) that all of the operations pertinent to the preparation of the requisite amount of sodium chloracetate has been complished, with the assurance (through the pressure switch C13) that an appropriate pressure of H_2S is available, with the assurance (through the pressure switch C11) that caustic soda solution is present in adequate supply, and with assurances that sulfuric acid is also present in adequate supply (through the pressure switch C26), the circuit from power supply through the holding coil of the relay C8 is completed. Through the power contacts of the relay C8, all members of the continuous product system are set into motion.

All conditions established by or upon the master switch C16 having been achieved, the relay C8 through its power contacts "H" proceeds to feed the sodium hydrosulfide solution stored in the sump E8 by means of the pump P4 to the reactor system. In consequence of this action, the float member of the level switch C14 is dropped to a position such that the contacts of C14 through the pilot switch C50 set the pumps P2 and P3 into operation. P2 is a proportioning pump delivering the caustic soda solution at a prescribed rate, while the pump P3 delivers water at a rate such that a dilution of the caustic soda solution from its starting concentration of commercial 50% caustic soda solution to approximately 1.11 lbs.

per gallon of water is obtained. The combined streams are homogenized by being forced to pass through a series of orifice plates forming an orifice manifold mixer, E19, and proceed thence to the absorption column. Simultaneously, and at a rate such that a pressure of 220 psi of H_2S is maintained over the solution, H_2S (composed of reclaimed H_2S from the H_2S Flash System and newly generated H_2S from the H_2S Generator) is fed from the Compressor, E17, to the absorption column. The operation of the Compressor, E17, is controlled solely by the pressure output switch, C17, athwart the circuit of the pilot switch for the compressor drive as shown in the wiring diagram for E17, to maintain 220 psig. of H_2S pressure over the absorption system. The heats of reaction between the H_2S and sodium hydroxide and of solution of the excess H_2S in the sodium hydrosulfide solution are absorbed by the recycling of a stream of chilled, finished sodium hydrosulfide solution from the Sump, E8, by means of the Pump, P8, through the refrigerated cooler, E20, to the top of the column, E7. This amounts to the blending of a finished stream of sodium hydrosulfide solution (from which sensible heat in equivalent quantity to the combined heats of reaction and solution in E7 is abstracted in E20), with the influent NaOH solution feed. During the passage of the blended streams down through E7 which is a lead-lined column packed with berl saddles, the influent NaOH solution is converted to sodium hydrosulfide and is saturated with H_2S to equilibrium with 220 lbs. of H_2S pressure at 20° C.

For a plant with an output capacity of 30,000 lbs. per 8-hour day, 25-day month of thioglycolic acid, there are employed:

1. A 10-HP, two-stage compressor, representing E17;
2. A 45-inch diameter by 6'0" height column packed with 1½" berl saddles; representing E7;
3. Using 40° F. freon as the refrigerant, a 167 sq.ft. heat exchange surface, uni-pass, "U"-tube type heat exchanger (representing E20) for the cooling of a 26 gpm recycle stream to the extent of 20° F. The refrigerant is handled on the tube-side of the lead-surfaced copper tubes while the aqueous product solution is handled on the shell-side of the exchanger.

In connection with the operation of the sodium hydrosulfide solution preparation system, there remains but to mention two pertinent factors:

1. H_2S gas is made available through the action of sulfuric acid on iron pyrites in an H_2S generator of conventional design.

2. In view of the facts that the corrosive action of wet H_2S represents a virtually insoluble problem from the standpoint of materials of construction for the compressor, E17, while dry H_2S represents no particular problem, a system comprising condensers E16 and E21, and the dryer, E22, is employed to assure that recycled, excess H_2S coming from the Flash System and the H_2S from the H_2S generator, E5, are thoroughly dried before delivery to the compressor, E17.

For a plant of the above stated capacity

1. Using an influent water temperature of 82° F. and a ΔT for the water stream of 40° F., a uni-pass, "U"-tube type heat exchanger (representing E16) with approximately 80 sq.ft. of heat exchange surface establishing an effluent H_2S gas temperature of 100° F. is employed; while a heat exchanger of the same basic construction by having 41 sq.ft. of heat exchange surface serves the purpose of E21, using 40° F. freon as an effluent product temperature of 50° F.

2. The dryer component (E22) of the system is of the activated alumina adsorption and regenerative type, and of conventional design. The function of the heat exchange bank is to reduce the mol fraction of water as a vapor of saturation in the H_2S gas to economic limits with respect to water and refrigeration costs, as well as with respect to the initial cost and cost-of-operation of the dryer equipment.

The Production of Sodium Thioglycolate

As previously observed, the preparation of the sodium hydrosulfide solution containing an excess of H_2S is a continuous operation which is carried out as one continuous operation in the company of the continuous operations to form sodium thioglycolate and to convert sodium thioglycolate to crude thioglycolic acid. Assuming therefore that the conditions established by and upon the master switch circuit have been satisfied, the agitator components of the Reactors E9 and E10 are set into operation through the closing of the contacts "Q" and "R" of the relay C8. Furthermore, the pump P4 feeding the sodium hydrosulfide solution and the pump P1 feeding the sodium chloracetate solution, through the closing of the power contacts "D" of C8, are set into motion. The streams from E8 and E1 representing the sodium hydrosulfide solution and the sodium chloracetate solution, respectively, are fed into a bank of reactors formed by E9 and E10. E9 consists of a heavy-walled, lead-lined tube capped at both ends, with a length-to-diameter ratio of approximately 6:1 down through the principle axis of which there passes, through a high-pressure stuffing box in one end of the tube's capped ends, an agitator shaft on which a multiplicity of equi-spaced paddle blades are mounted. The blades apply a rotation couple to the mass in the reactor against the braking action provided by a set of baffle fins attached to the internal wall of the reactor tube and running the entire length of the tube.

The combined effects of the feeding of the sodium chloracetate solution at 50° C. and the heat-of-reaction engendered in the reaction between the sodium hydrosulfide solution and the sodium chloracetate will, under moderate conditions of insulation of the reactor, E9, against loss of heat by radiation and convection, insure an effluent reaction stream temperature of approximately 94° F. The use of the 6:1 ratio of length to diameter for the reactor and the use of agitation by the application of a simple rotation couple by paddle blades (with no propelling component in or against the direction of mass flow) provides for a minimizing of end-to-end blending of the reactors' contents and hence a maximum simulation of a simple displacement type of flow through the reactor.

In providing for a displacement type of flow as opposed to a homogenizing of the contents of the reaction stream, the hold-up time within the reactor, E9, is minimized since the effects of dilution of the influent streams by the highly reacted material at the discharge end of the tube is avoided. The reactor, E10, is identical in construction with E9, except for the fact that the cylindrical portion of the reactor is jacketed for the application of steam heating of the vessel's contents. Through the heating of the reactor, E10, by way of the jacketed surface of the vessel as previously mentioned, an effluent reaction stream temperature of 115° F. is obtained.

The conditions of design for E9 provide for an average retention time within that reactor of ten minutes, while the conditions of design of E10 provide for a retention time within that unit of approximately three minutes. The bulk of the reaction takes place in reactor E9 with reactor E10 serving as the point at which advantage is taken of the increase in the reaction velocity coefficient for the reaction resulting from the application of higher temperatures, thus assuring the quickest possible completion of the reaction against the normally retarding factor of dilution of the reaction streams. The conversion to sodium thioglycolate is, at this point, approximately 97% of theoretical, based on the amount of chloracetic acid employed.

The Conversion of Sodium Chloracetate to Crude Thioglycolic Acid

The effluent stream from the reactor E10 passes to E11 through the valve, V12, which is regulated by the pressure instrument, C33, to maintain a constant back-pressure on the previous portion of the system. Since the pressure over the system in the H_2S Flash Column, E11, is maintained at slightly above atmospheric, the passage of the reaction stream across the valve V12 involves the flashing of the bulk of the excess H_2S. That portion of the H_2S which is immediately relieved on the down-stream side of valve V12 enters the foam separator, E13, where a separation of the gas and the vapors-of-saturation contained therein from entrained liquid is effected, the liquid returning to the line by which it flows into the unit E11. The immediate zone, the "free" zone, in the column E13 into which the line down-stream from valve V12 enters is an empty space bounded at the upper end by a perforated plate supporting a two-foot height of berl saddles, and bounded at the lower end by the top surface of a column of randomly-packed berl saddles stretching from the bottom of the column to a point as equi-distant from the point of entry into the column as the above-mentioned perforated plate. This "free zone" acts as a disengagement space for the two-phase stream which enters K11. Into the packed zone above the free zone there is effected a constant rate feed of 60% sulfuric acid in quantities slightly in excess of that required to react with the excess sodium hydrosulfide solution, and sufficient to convert the sodium thioglycolic acid content of the entering stream to thioglycolic acid. The combined effects of the low solubility of H_2S in an acidic stream along with the application of heat through an internal coil located in the packed zone beneath the free zone is sufficient to secure an elimination to negligible dimensions of excess H_2S from the effluent crude thioglycolic acid stream.

The mixing of the sulfuric acid with the influent sodium thioglycolate stream is accomplished principally in the packed zone beneath the free zone. The liquid effluent from the H_2S flash column will, under proper design conditions, have a concentration of 1.225 lbs. of thioglycolic acid per gallon of solution, and will contain sodium chloride, sodium sulfate, excess sulfuric acid as its main impurities as well as chloracetic acid and dithioglycolic acid as trace impurities. This liquid effluent passes from the flash column to the sump, K12, where it is maintained at a temperature of 170° F., through the action of the temperature instrument, C37, controlling the input of steam by way of control valve V13 to the internal coil in K12. The intermittent exhausting of the contents of K12 to the crude thioglycolic acid storage K15 is effected by the level control instrument, C23, which is identical in its principle mode of operation with that of the level instrument, C3. The intermittent "pumping-down" of the contents of K12 to the minimum level controlled by the instrument C23 is effected through the delivery of the signal from C23 to the pilot switch C24 in the circuit of the drive for the pump P5 and through the simultaneous delivery of the signal from C23 to the valve V4 as set forth in the wiring diagram for K12. The effluent H_2S from the Flash Column K11 and the Foam Separator K13 are joined up and passed to the condenser and dryer system on the up-stream side of the Compressor K17 for the purpose previously described, prior to the recharging of the absorption column K7 with the

the recycled H_2S by the compressor K17. The recycled H_2S is joined with fresh H_2S from the H_2S generator at the inlet point of the condenser, K16. Control over the rate of H_2S make-up by the H_2S generator, K5, is by way of the pressure instrument C12. The flow of refrigerant fluid to the condenser K21 receives its starting impulse from the closing of contacts "S" in the relay C8, after which the temperature instrument C49 measuring the temperature of the effluent gas from K21 becomes the conditioning factor.

For the plant capacity named above, the Flash Column is 1½ ft. in diameter, is packed with 1" berl saddles to a height of 10 ft. beneath the "free zone", has an overall "free zone" height of approximately 4 ft., and a packed zone above the "free zone" of 2 ft. The sump component of the system is furnished by an 18 in. diameter x 24 in. straight-side chamber which is provided with ten turns of 1 in. lead-coil on a 12 in. mean diameter. Both the Flash Column and the sump are of lead-lined construction.

THE PRIOR ART

Thioglycolic acid is generally prepared commercially by the reaction of chloracetic acid with thiourea to form a thiouronium complex which is then decomposed by heating with an alkali to sodium thioglycolate, after which the sodium thioglycolate is converted to thioglycolic acid by treatment with a mineral acid. This process suffers from several disadvantages of which one of the greatest is the high cost of thiourea. This disadvantage is aggravated by the fact that 44 parts by weight of the thiourea is converted to cyanamide and other irrecoverable products for every 32 parts by weight which appears in the finished product. That is to say, the only part of the thiourea molecule, $(NH_2)_2CS$, which appears in the thioglycolic acid is the sulfur atom.

In spite of the disadvantages of the thiourea method, the alternative method of reacting sodium hydrosulfide with chloracetic acid has not been used industrially because it has had even more serious shortcomings.

Klason and Carlson (Ber., 39, 732 (1906)) prepared thioglycolic acid by adding a solution of chloracetic acid to a 15% potassium hydrosulfide solution containing 2 moles of hydrosulfide. The second mol of hydrosulfide is required to convert the chloracetic acid to its potassium salt. Klason and Carlson state that the chloracetic acid can first be neutralized with alkali and the solution of the salt added to one mol of potassium hydrosulfide. In small trial experiments they claim they obtained yields ranging from 57.7% using 50% potassium hydrosulfide and 0 parts water per part of chloracetic acid to 99.6% using 15% potassium hydrosulfide solution and 7 parts of water per part of chloracetic acid. They state, therefore, that higher dilutions favor increased yields. The yields they describe seem to be greatly exaggerated (see examples 1 and 2, which are appended hereto as illustrative of the general technique used by Klason and Carlson). A possible source of error (the method of determining the yield is not stated) is the determination of hydrogen sulfide as thioglycolic acid, the amount of dissolved hydrogen sulfide increasing with the amount of water, and the apparent yield therefore increasing with dilution of the reaction mixture.

Schütz (Angew. Chemie, 46, 780-1 (1933)) claimed a 99% yield of pure thioglycolic acid by adding an aqueous solution of chloracetic acid to a solution of sodium hydrosulfide saturated with hydrogen sulfide. Previous investigators had obtained very poor results by this method. Schütz attributed his high yield to the use of sodium hydrosulfide which had been freshly prepared by passing hydrogen sulfide into sodium hydroxide solution. He stated that the sodium hydrosulfide of commerce had deteriorated so much because of atmospheric oxidation that it was unsuitable for the preparation of thioglycolic acid in high yield. Among the claims made by Schütz is the claim that no hydrogen sulfide is evolved during the addition of the chloracetic acid solution to the hydrosulfide solution. This is a very unexpected result since the addition of a comparatively strong non-volatile acid such as chloracetic acid to a solution of a salt of a weak, volatile acid such as hydrogen sulfide should result in the evolution of gas according to the following:-

$$ClCH_2COOH + NaHS \longrightarrow ClCH_2COONa + H_2S\uparrow \quad (4)$$

In fact, we have found, on repeating the procedure described by Schütz, that a vigorous evolution of gas takes place throughout the addition of the chloracetic acid. Furthermore, we have found that the yield of thioglycolic acid obtained by this procedure is actually in the neighborhood of 20% instead of 99% as claimed by Schütz.

Because of the extremely poor yields obtained in the past by the sodium hydrosulfide method and because of the inconvenience associated with its use, it has not been used for the commercial preparation of thioglycolic acid in spite of the low cost of the starting materials and the directness of the method. By our invention we have succeeded in eliminating the objections to the method.

The claims of Schütz are manifestly absurd in view of his statement that no evolution of H_2S was observed upon contacting freshly-prepared sodium hydrosulfide solution with chloracetic acid. In view of the relative magnitudes of the ionization constant of chloracetic acid (namely 1.5×10^{-3}) and much lower dissociation constant for H_2S (9.1×10^{-8} for the first ionization — $H_2S \rightleftharpoons HS^- + H^+$; and 1.2×10^{-15} for the second ionization — $HS^- \longrightarrow H^+ + S^=$) and the limited solubility of H_2S in salt solution, Schütz' specific comment in this direction brands the whole character of his work, since by all the laws of physical chemistry the reaction

$$ClCH_2COOH + NaHS \rightleftharpoons H_2S\uparrow + ClCH_2COONa \quad (5)$$

could have no other basis for shifting in the left-hand direction than that the above-stated relative magnitudes of dissociation be of reverse order.

The work of Klason and Carlson, at least superficially, is of a higher order than that of Schütz and shall be so treated below in connection with our statement of claims.

THE CLAIMS

The roots of our invention lie separately in the novelty of the engineering features and the novelty of certain aspects of the chemistry, as well as in the intertwining of the chemical and the engineering features of the invention. These points of novelty are:

1. Operation under a "super-atmospheric pressure of H_2S

The replacement of chlorine by a sulfhydryl group to form thioglycolic acid from chloracetic acid differs from the conventional mercaptan synthesis from alkyl halides in that a chlorine atom in the alpha-position to a carboxyl group shows a greatly enhanced reactivity. This enhanced reactivity increases the possibility of side reactions. It is therefore generally conceded that the principal deterrent to high yields of thioglycolic acid by the hydrosulfide-chloracetate salt technique lies in the side-reactions to produce dithioglycolic acid as per the following:

$$\text{GROUP A}\left\{\begin{array}{llr} HS^- \rightleftharpoons S^= + H^+ & & (6)\\ 2Na^+ + S^= \rightleftharpoons Na_2S & & (7)\\ NaSNa + ClCH_2COONa \longrightarrow NaCl + NaSCH_2COONa & & (8)\\ NaSCH_2COONa + ClCH_2COONa \longrightarrow NaCl + NaOOCCH_2SCH_2COONa & & (9) \end{array}\right.$$

$$\text{GROUP B}\left\{\begin{array}{llr} NaHS + HSCH_2COONa \longrightarrow H_2S + NaSCH_2COONa & & (10)\\ NaSCH_2COONa + ClCH_2COONa \rightleftharpoons NaCl + NaOOCCH_2SCH_2COONa & & (9) \end{array}\right.$$

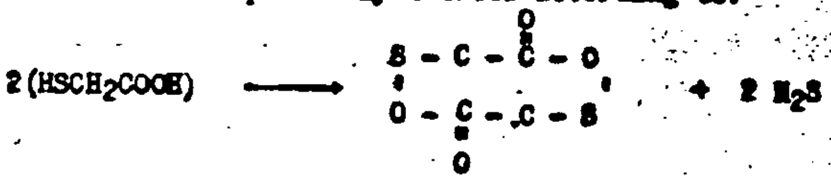
and the variants thereon. With respect to Equation (6) which is basic to the production of $NaSCH_2COONa$ via Equation (8), it is apparent that the excess of H_2S present in our system in consequence of the "super-atmospheric" pressures of H_2S employed by us in preparing the NaSH solution produces the contending phenomenon to (6), namely: $S^= + H_2S \rightleftharpoons 2HS^-$. Similarly, in Equation (10) which is basic to the second-named means of forming $NaSCH_2COONa$, we find, by viewing the right-hand side of (10), that the excess of H_2S would displace the reaction in the opposite direction. Thus the two paths of approach to the formation of $NaSCH_2COONa$, and hence to the formation of the ether compound side-reaction product, are effectively blocked by the use of the large excess of H_2S in the system.

At this point, we do well to mention the work of Klason and Carlson. The validity of the mechanisms proposed in Equations (8) and (10) are too well based on the distinguished acidity of the hydrogen atom of the sulfhydryl to warrant contradiction. Moreover, the relative irreversibility and existence of the reaction in Equation (9) is not open to question. Hence, the existence of the ether-forming side-reaction as the principle side reaction is beyond doubt. Klason and Carlson stated that the great dilution of their system, for a 99.6% yield, favored the hydrolysis of the $NaSCH_2COONa$ to $HSCH_2COONa$, thereby defeating the reaction according to (9). It is self-evident that this is possible. But it is important to observe that this takes place at a tremendous sacrifice in dilution of his final solution with respect to the thioglycolic acid. This would mean a concentration of acid, prior to treatment of the sodium thioglycolate with acid of 0.51 lbs. of thioglycolic acid per gallon of final solution. Since the final product must be isolated by extraction from aqueous solution and distillation (if desired in pure acid form) or extraction from aqueous solution with an organic solvent plus a subsequent extraction of the organic solution by an aqueous alkaline solution (if desired in its pure salt form) it is apparent that the isolation of the final product from the original crude is a much more difficult task than in our case where we produce a far more concentrated crude. This is especially true in view of the extreme solubility of thioglycolic acid in water, and the consequent poor distribution coefficient between the extracting organic solvent and the crude aqueous solution.

2. The Use of a Continuous Mode of Manufacture

Granting, as demonstrated above, the desirability of employing a sodium hydrosulfide solution which is surcharged with excess H_2S to the maximum possible extent, the greater the excess of H_2S (and greater concentration than that given for the illustrative plant would be desirable[1]) present the more logical does the continuous method of manufacture become. The conclusion arises from:-

1. The fact that in any case production of thioglycolic acid involves a dilute system with respect to the thioglycolic acid content of the final crude solution. The manufacture of thioglycolic acid in highly concentrated crude solutions risks the formation of lactide and polymeric derivatives respectively thereof according to:



$$2(HSCH_2COOH) \longrightarrow \begin{array}{c} \overset{O}{\overset{\|}{}} \\ S - C - C - O \\ | \qquad\qquad\quad | \\ O - C - C - S \\ \underset{O}{\underset{\|}{}} \end{array} + 2\,H_2S \qquad (11)$$

$$(n)HSCH_2COOH \longrightarrow (n-1)\,H_2S + HSCH_2CO\,(SCH_2CO)_{n-2}SCH_2COOH \qquad (12)$$

While it is true that such lactides and polycondensation products would be susceptible to saponification, the act of saponification would of itself involve a dilution of the final product.

The batch execution of the above-mentioned process requires an unusually large, and therefore extremely expensive, autoclave for the magnitude of pressure involved. Despite the short reaction time required, a decision to employ a multiplicity of batches per day to reduce the size of clave needed would run afoul of the fact that the relieving of the mass of its excess H_2S would, for a short cycle of relief, involve tremendously large absorption equipment; or, for an extended cycle of relief, would impose a long "dead cycle" (with respect to the actual task of the vessel which is reacting). A decision to circumvent these objections by passing the reacted mass to a storage point from which it would be doled out to the H_2S flashing equipment, would build up the amount of expensive pressure vessel equipment involved in the plant.

2. From the number of controls applied to the continuous plant as shown on the accompanying flowsheet, it is apparent that there exists a multiplicity of opportunities for failing to impose optimum conditions upon the process. These disastrous opportunities arise from the nature of the chemistry involved, which is complicated, and is therefore implicit in the chemistry rather than in the plant design.

The enlarged opportunities for instrumenting continuous type plants for the maintenance of steady-state, and therefore, constantly-held conditions as compared with the ability to impose automatic control on the variable conditions involved in batch-type operation, argue again in favor of the use of continuous type production and is related to the nature of the chemistry involved. Funthermore, in connection with the subject of in-

---

[1] Patent protection for operation in liquid H_2S as a solvent material, exclusive of the water entering the system with the sodium chloracetate solution, and for a system involving a reaction between molten sodium chloracetate and NaHS in in liquid H_2S should also be requested.

strumentation, the enlarged opportunities for instrumentation of a continuous type plant mentioned above also mean that an enormous savings in manpower per unit pf production can be effected, thereby minimizing the cost of production of this material.

It is important to observe that while in the plant which we have designed, a failure at any one point means the discontinuation of operation of the entire plant, thus eliminating the possibilities of "carrying the error" from one point to another, a failure at any point in the operation of a batch-type system would involve the carrying of that failure to its ultimate conclusion to the rest of the processing sequence.

The effect of continuous-type production (with its susceptibility to constant and automatic control) on uniformity of end product from day to day is almost too obvious to warrant further discussion.

3. In addition to the general economy involved in smoothly spreading surge loads,with respect to both chemical and chemical thermodynamic inertias, such as are involved in a process of this type over a period of time and thereby enabling the use of smaller size equipment for each of the individualized tasks, there exists the added consideration that the continuous process lends itself unusually well to the exclusion of air from the system which, in the case of thioglycolic acid, would involve a deterioration of the end product if the exclusion of air were not provided for. Again, in view of the excess of H_2S employed by the process and the consequent necessity for relieving the same from the system at the end of the process, the continuous production method, with its constant and equalized trading between units carrying out individualized tasks permits of the easy recycling of the excess H_2S without, at any point, necessitating venting to the atmosphere of this material even when shutdown operations are involved.

ADDITIONAL CONSIDERATIONS

It might also be well to attempt to get proéection on the system of ideas involving the following:

1. A reaction between molten sodium chloracetate and sodium hydrosulfide in liquid H_2S solution, in which a far more concentrated end product resulting in the formation of the polymeric and lactide forms of thioglycolic acid are the end products of the reaction.
2. A subsequent operation in which the polymeric and lactide end products are saponified with ammonia hydroxide, sodium hydroxide, calcium hydroxide or any other alkaline aqueous medium to produce the salts of thioglycolic acid.

EXAMPLES

1. Reaction under atmospheric pressure: A solution of 42.5 g. sodium hydroxide in 350 cc. water was saturated with hydrogen sulfide at 21° C. A solution of sodium chloracetate prepared by dissolving 95 g. chloracetic acid in 200 cc. water and adding 53 g. sodium carbonate was added slowly with the temperature being kept below 28° C. by cooling. After all the sodium chloracetate solution had been added, the reaction mixture was warmed to 95° C. during a period of one-half hour and slowly cooled to room temperature. Titration of a sample after acidifying with sulfuric acid indicated a 60% yield of thioglycolic acid.

2. A solution of 22 g. sodium hydroxide in 150 cc. water was saturated with hydrogen sulfide at 5° C., while cooling in an ice bath. To the sodium hydrosulfide solution thus prepared there was added a solution of sodium chloracetate prepared by dissolving 47.5 g. chloracetic acid in 100 cc. water and adding 26.5 g. sodium carbonate. The temperature of the reaction mixture was kept at or below 5° C. during the addition and a slow stream of hydrogen sulfide was passed through. After standing at 5° C. for two hours the reaction mixture was warmed to 50° C. for one-half hour. Titration of a sample indicated a yield of 61.5%.

65-4307

Ex 20

SAC, Philadelphia

SA T. SCOTT MILLER

HARRY GOLD, was.
ESPIONAGE - R

7/10/50

EXHIBIT 65-4307-1B-13 (9) (Exhibit 20)

On 6/22/50, GOLD examined this material, at which time he stated that the notes dated in November of 1946 were in his handwriting and were concerned with literature work in the library by GOLD on the oxidation of dimethyl hexine diol, which process the BROTHMAN firm was working on.

GOLD stated that the material in the tablet is in his handwriting and is concerned with the diol process above.

The notes dated 11/20/47 are in GOLD's handwriting and are literature searches on a formula for the decomposition of acetate and relate to a projected process for the production of methyl alcohol. This was done for the BROTHMAN firm by a man in Brooklyn.

The single sheet of paper dated 11/2/47 was work in connection with the process for making a high test bleach for the METTUR CHEMICAL COMPANY of India.

The letter dated 12/3/47 was merely in connection with business of the BROTHMAN firm.

GOLD was unable to identify the notes on the small piece of yellow paper but stated that the notes were in his handwriting.

TSM:HKF
65-4307

HE GIRDLER CORPORATION
INCORPORATED
P. O. BOX 987
LOUISVILLE 1, KENTUCKY

FIRST CLASS

THE GIRDLER CORPORATION
224 E. Broadway · Louisville 1, Kentucky
Votator

A. Brothman and Associates,
Chemical and Mechanical Engineers,
85-03 — 57 Avenue,
Elmhurst, L.I.

Attention: Mr. A. Brothman, Chief Engineer.

3-5-48
Mellor XI. p.545

MoO_3

Sol. 0.2 gm / 100 H_2O @ 18°C ~ at r.t.

Hydrates not more soluble.

0.2 cold → 0.5 at 80°C

3-5-48

OsO_4 . Ref. Mellor $\overline{XV}$ p. 707.

Prepn.

1. Heat finely divided Os in air at 400°C
2. OsO_2, OsO_3 and Os_2O_5 readily go to OsO_4 (volatile) on heating in air.
3. Boil aq. soln of K osmate → volatile OsO_4.

Reaction. Behavior

1. OsO_4 acts to influence rate of decompn of alkali chlorates. But M. says it is due to the formation of an addition cpd. (Gives 3 reasons)
2. OsO_4 soluble 0.47 gm in 100 HOH at 18°C
   OsO_4 soluble 250 gms in 100 CCl_4 (but distrib. with HOH decreases on addition of alkali)

$MnSO_4 \xrightarrow{aq.} Mn_2(SO_4)_3$ Mellor $\overline{XII}$

$\xrightarrow[MnO_2]{aq.} HMnO_4$

Mellor $\overline{XII}$ p. 158

Mn ous salts not influenced by atmos. O

- $O_3 \rightarrow MnO_2$
  [illegible] → [illegible]